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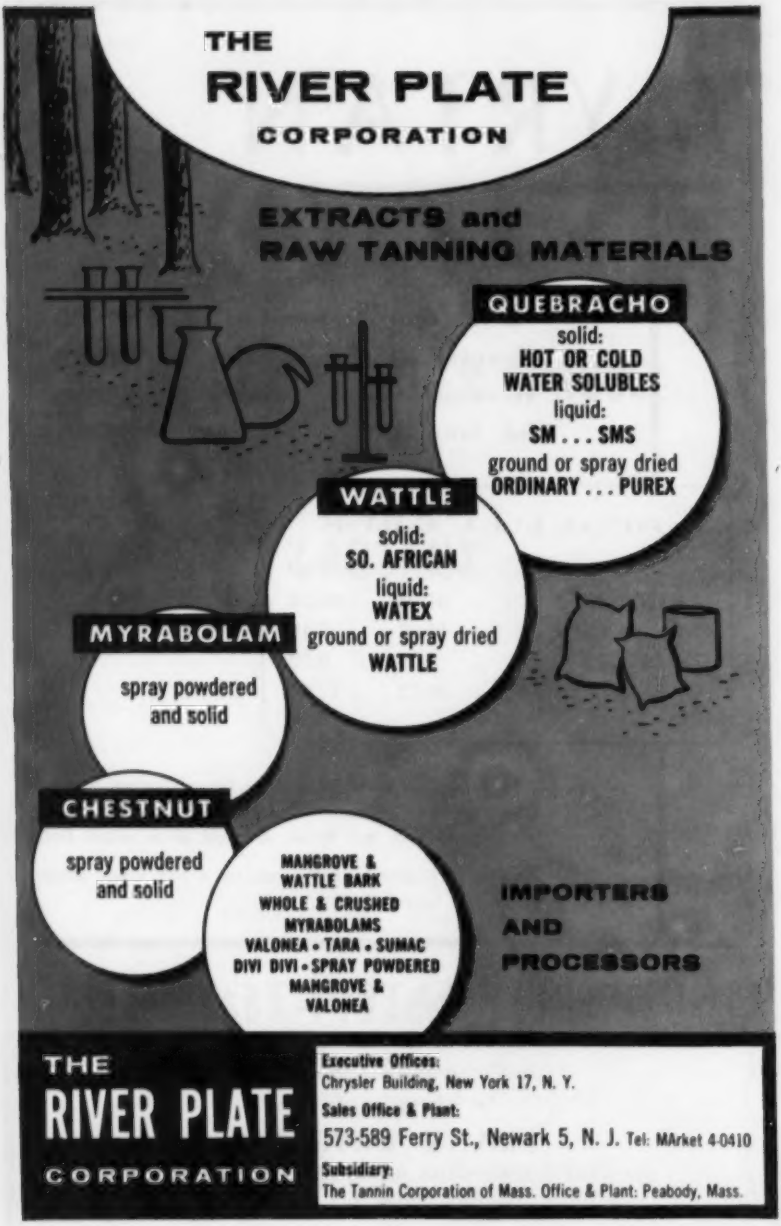
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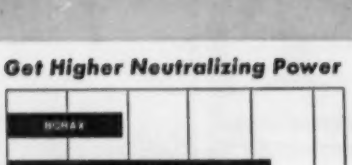

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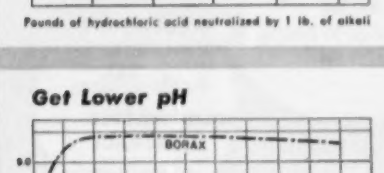

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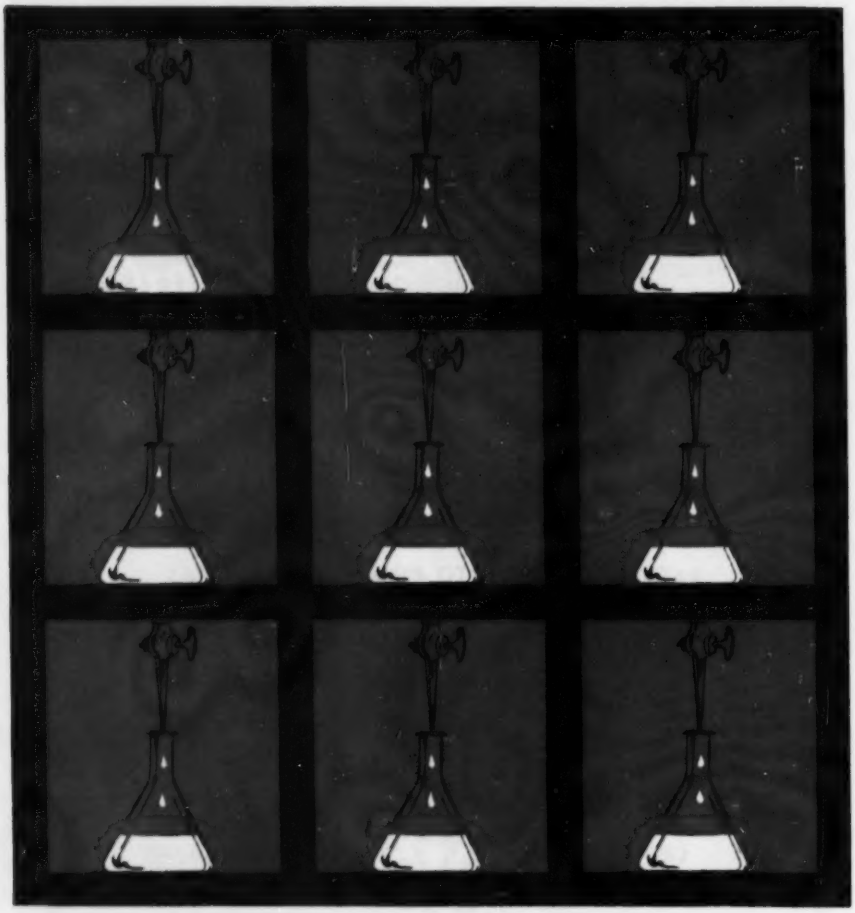

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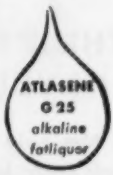

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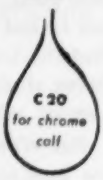

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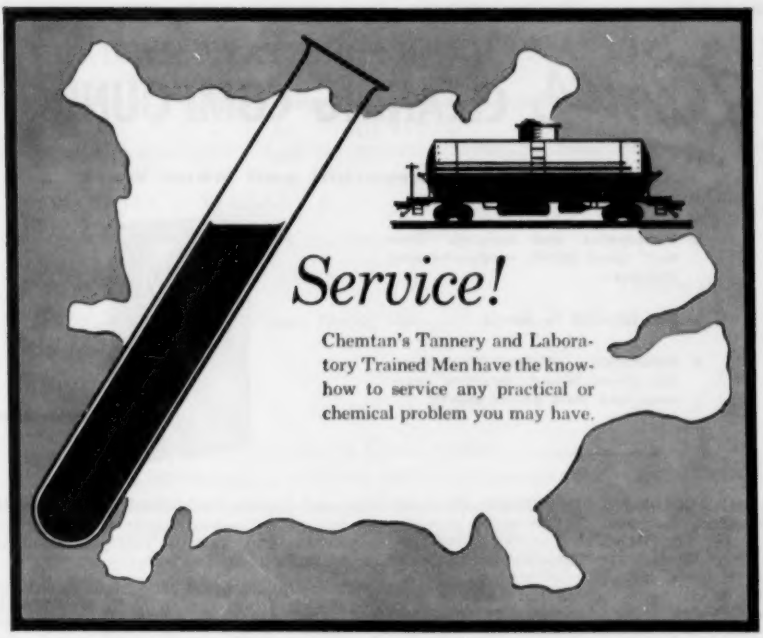
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J. Howard Stuewe
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Beamhouse Problems Concerning the Production of Vachette Leather*

DR. HELLMUT GNAMM

Stuttgart–Feuerbach
West Germany

Translated by
Theodore D. Braunschweig
Moorefield, West Virginia

INTRODUCTION

This year, in arranging the program for its annual convention, the Verein für Gerberei-Chemie und-Technik has departed from previous custom. The floor, for once, has been given exclusively to the practical men to point out some of the problems which present themselves continuously in the beamhouse. Since I have the honor of being the first speaker, I may, without anticipating any of the later speakers, start with a few general remarks.

It is a most welcome coincidence that the American Leather Chemists Association, at its convention last year, organized a "round-table discussion" equally pertaining to problems of the beamhouse. These discussions with speakers of 29 companies participating have been published in the U.S.A. That round-table discussion differs fundamentally from what we have in mind for today. The Americans, right from the start, had been informed that there should be no prepared speeches but that it was expected that in a free discussion all participants would present their opinions and experiences at their discretion.

We intend to do differently and, in my opinion, more appropriately. The VGCT has asked some practical tanners to voice their opinion on "Problems of the Beamhouse" in the manufacturing of specific types of leather—and to do so in the form of a lecture. Thus the discussion, which in the American forum sometimes flowed too freely and occasionally switched suddenly from one problem to another, in our case would be within a defined frame. We hope that later on in the discussion you will present your own experiences with the same frankness—pro or con—as it was done in America. While the openness of the Americans in discussing the procedures in their plants is quite surprising to us, we cannot overlook the fact that even there some questions were brought forward to induce speakers to say, "This point I would rather not discuss". It is understood that there are limits which cannot be transgressed.

* An address delivered at a meeting of the Verein fur Gerberei-Chemie und-Technik E. V. in Darmstadt on September 16, 1955. This paper, originally published in the November, 1955 issue of *Das Leder* is translated and published by permission of the author and the editor.

The German expression "vachette leather" includes a great variety of vegetable-tanned leathers, e. g., case, bag and strap leathers, harness and saddle leathers, furniture, upholstery and automotive leathers; for simplicity, the translator has retained "vachette" to characterize these various types of leathers in one word.

Today, we have not much use any more for the expression, "Leather is made in the beamhouse." Tanning and, even more so, finishing form equally important parts in the process. Yet the beamhouse is still the basis for leather manufacturing.

It is not possible to discuss all pertinent problems in the short time of one hour; in my paper I can only present a few selected problems of the beamhouse.

THE PRINCIPLE OF THE SPECIFIC FACTOR

We have available voluminous literature in the form of books and periodicals in all languages. Authors of greater or lesser competence have tried in manuals, compendiums, and pocket editions to lay down somehow the state of our technology at a given period. The more voluminous such an encyclopedia, the more numerous the authors participating in its composition and by their number delaying its publication, the more it becomes ripe for a museum. Periodicals, however, inform us through technical, technical-scientific, or purely scientific presentations about the newest results of research in tanning chemistry and technology. Now, do we find in such literature a discussion of the problems which I have in mind today? Yes and no. *Yes* in small and *NO* in capital letters. Yes, inasmuch as such problems are mentioned at all. We find anything and everything that scientific and technological research can say about such problems. Chemical analyses are made of all materials which act in some way on the yet little-known collagen fiber called rawhide, and the laws which govern such reactions are investigated. Comparative tests are made with various types of skins, and frequently laboratory tests, which tell so little, are abandoned in favor of whole packs of hides. Certainly all research on such a chemical- or technical-scientific plane leads to certain solutions. Yet, you will ask why I put next to the *yes* such a capitalized *NO*. You will find the answer in my following explanations.

I would first like to select a point from the American round-table discussion to show you, by the treatment it received in the American forum, what I understand today by "problems". There was, among others, the question, What causes formation of a drawn grain on a white hide? In parenthesis, I would like to mention that a "drawn grain" naturally has nothing in common with "loose grain". The following divergent opinions were brought forward:

1. One will find more drawn grain in a very sharp lime of short duration than in a less sharp lime of longer duration.

2. Cases of heavily drawn grain have been observed in mildly sharp limes.

3. Drawn grain is a function of the alkalinity of the unhairing solution.

4. Drawn grain has nothing to do with alkalinity because there is hardly any drawn grain in "pasting" in spite of the added NaOH.

5. Drawn grain is caused by too much soak before liming.

6. Drawn grain is caused by deliming and bating in the same process.

7. Drawn grain is caused by washing for any length of time between unhairing following additional liming.

You can see how widely the opinions on drawn grain differ as to its causes. And by attempting other explanations, a solution of the problem becomes less probable for all practical purposes simply because the phenomenon of a drawn grain does not have one and the same cause in different tanneries. This is appropriately expressed in a remark made by one of the speakers in the discussion: "After I have listened all morning to the discussion of a lot of questions I would like to say that there is a lot of truth in the old saying, 'There is more than one way to skin a cat.' " In other words, technical problems in manufacturing leather, and in particular as far as the beamhouse is concerned, are bound in each single plant in the tanning industry to a very definite, local, "specific factor" of the plant in question which makes the problem "our own problem".

For this reason, the beamhouse problems are different for each individual plant. This also holds true for plants making an identical type of leather. And once we start to consider the problems which arise in processing different types of leather within the same plant, a conversation concerning "beamhouse problems" becomes extremely complicated. Surely, it is not possible to install a separate beamhouse with special soaking and liming for all these various types of leather. For reasons of practical efficiency it is imperative to get along with a liming procedure of general suitability. Anyone who wants only to make a good "vachette leather"—and vachette leather means upholstery leather as soft as cloth as well as luggage and case leather with a certain firmness—already has enough beamhouse problems. But if such a plant manufactures a variety of different types of leather, not even in several hours would it be possible to discuss all its beamhouse problems. To tackle the specific problems of such tanneries in their complexity, with their irregular appearance, with their increases or decreases, with their contradictory consequences, with their interlacing with problems in other sectors of the plant, one needs years and years of experience.

Even now we run into some phenomena in everyday occurrences when our technical plant superintendent, who has been with us for 36 years, and myself at times have to admit in all honesty that we just cannot imagine the cause of the phenomena. Thus it is not surprising that outsiders are even less apt to be of assistance.

In comparing liming methods in identical plants in the tanning industry like side leather or upholstery leather tanneries, as they come to us from

the U.S.A. through the aforesaid round-table discussion or through other information and reports, one finds a variety of working procedures. One hears about short and long vat liming and about hides in suspension or in layers; one finds any degree of sharpening with sodium sulfide and sulfhydrate, alone or in varying proportions; one finds liming in drums, in paddles, great variations in temperature and time, and finally one finds very definite statements that a liming procedure had been found practical in plant A and useless in plant B and vice versa. If, for example, a certain side leather tanner states that he is abandoning his vat liming process which he had been using for years in favor of drum liming, then we have gone just the other way around. Thirty years ago, we limed in vats but changed over to drum liming about 25 years ago. After a few years however, we abandoned the drum liming and for 20 years we have now been liming again in vats. So far I have been trying to explain the importance of what the American means by "our own problem" or what I have in mind by stressing the "specific factor of a plant". Suggestions for making leather with tight or flat grain or leather with a fiber as soft as cloth or with a certain feel or stand can be found in books. This, however, is not what we have under discussion. My particular question is: What are the beamhouse problems in a tannery where there is a very definite "specific factor", where with other types of leather as a side line, the main production consists of bag, case and strap leather—a leather which besides the characteristics I just mentioned should also have a spotless grain so that it can be used without difficulties for strictly aniline-dyed colors?

BEAMHOUSE PROBLEMS IN THE VACHETTE TANNERY

The question of split utilization is closely connected with the manufacture of vachette leather. For upholstery leather, for instance, we use mainly heavy bulls or steers of 90 lb. and over. How should such raw stock be limed if the grains are to be made into upholstery leather with a velvet-soft feel and the split is to be used for firm chrome sole leather or for solid-white chrome split sides for sports shoes or for vegetable flexible splits?

The same problem arises in liming medium or light bulls and cows to be manufactured into billfold, briefcase, case and similar leather for the novelty trade, as well as into the various split types I just mentioned. At this point I cannot by pass another tangent problem, the raw stock problem which I have not as yet taken into consideration. In former times, it was self-evident that one selected the best-suited raw stock for the various types of leather. Today for reasons of rentability, this is no longer so easily accomplished. The tanner in general knows very little about his raw stock; in particular, he is not sure about the time which elapsed between the butchering of the animal and the start of curing the hide. Even less does he know about imported hides, how long the hides had to wait before curing and what effect on the hide resulted from this unkown time interval, perhaps in warm summer

climate and with improper storage. He does not know the cause of the defects which most of the time show up only on the finished leather, as far as the cause is to be looked for outside the tannery. A plant in which vachette leather is processed besides other types of leather is requested not only to make a leather with a tight or a low, smooth grain or, according to the desired use, a leather with a cross grain or with a particular feel, but also to make a leather which possesses all such characteristics at the same time and on top of all has such a clean grain that it can be colored faultlessly with aniline dyes. Now I have named just a few problems which appear besides many others if one makes a change in the beamhouse to modify one characteristic of the leather without disturbing the other characteristics.

From the various problems I have just mentioned I want to pick out two which are connected with the beamhouse procedures: loose grain and cleanliness of the grain for aniline coloring. The term "aniline coloring" here applies to the finishing of vegetable-tanned leather by use of water-soluble dyes without addition of pigments of any type. To understand the specific factor of our plant where I have learned about these two problems I must add the following information:

1. Tannery water: from a well 330 ft. deep, with 750–780 ppm total hardness of which about 430 ppm permanent hardness (calcium sulfate), and free of bacteria. Temporary hardness is removed in some parts of the beamhouse. Formerly water with 1500–1875 ppm permanent hardness (saturated $CaSO_4$-solution).

2. Location of the tannery: Stuttgart-Feuerbach with its climatic conditions.

3. The tannery has been in the same location since 1872, more than 80 years. During these years, the plant was enlarged some 20-30 fold. The beamhouse was converted from a bleak recess which was customary at the end of the last century into a 20-times larger modern hall.

4. Production program:
   Vachette leather (*a*) very soft for upholstery
   (*b*) with more or less stand for the novelty trade
   Strap and harness leather; welting leather
   Belting butts as well as other mechanical leathers
   Chrome sole leather and chrome sole splits
   Chrome belting leather
   Chrome vachette for mechanical specialties
   Vegetable-tanned flexible splits
   White chrome splits for sports shoes
   Other leathers as required.

5. The raw stock problem depending on the production program.

6. It is self-evident that the "specific factor" of a plant is influenced by the labor force and the supervisors in charge, and by the mechanical equipment and installations, as well as by the changes caused by the efforts to increase rationalization.

LOOSE GRAIN

I start with the all-important and unpleasant problem of loose grain. Anyone who has anything to do with leather knows how a loose or piping grain looks. The chemically known causes are marked sensitivity of the part, or rather the zone of papillar layer which borders the reticular layer, towards the effects of bacteria, and ferments and chemicals present in liming. This zone of the hides is characterized by numerous little cavities which originate in the hair roots and follicle sacs. The susceptibility of this zone is different among the various types of hides and, furthermore, changes at various locations within the same hide. Best known is the loose grain in the flanks of the raw stock. In this spot the structure of the hide fibers is much looser than in other hide locations. This can be verified by the ease of dislocating the papillar over the recticular layer. This phenomenon in itself has nothing to do with the problem of loose grain. Only when this dislodging of the grain spreads out over the surface of the hide does the problem start. What research so far has been able to say about the causes of loose grain on leather is compiled very clearly and in a well-arranged form in the book of F. Stather *Haut- und Lederfehler* (*Hide and Leather Defects*), 2nd edition, pp. 100–103.

Most difficult to control is the effect of bacteria on this critical hide zone. I have already intimated that we do not know anything about the invisible process triggered or started by bacteria before the hide goes into processing. In wintertime this influence is less effective than in summer when it may become quite dangerous. In processing of imported raw stock this factor is most uncertain. Our best protection against this invisible enemy is our water, free of bacteria and quite hard, in which the hides are soaked and which, at all times, is used only when fresh. The water has a natural temperature of 14°C. which during the summer may rise in soaks and limes as high as 23°C. Such temperatures, on one hand, are very favorable for a thorough soaking but, on the other hand, increase the danger from bacteria if any are present. Such temperatures would be even more dangerous if we had soft water. Constant use of disinfectants is costly. Shortening of the soak by paddling as is frequently done in the U.S.A. results in a considerable mechanical strain on the hide which we do not welcome. Our water of 750–780 ppm total hardness permits a sufficiently long soak of the hides for vachette leather. We know very well that our water has a delaying effect on the beamhouse processes. This effect gives a peculiar note to our whole beamhouse procedure which we value highly, for instance at times of extended beamhouse operations during holiday periods.

The thorough soak required for vachette leather is ascertained by adjusting winter temperatures to average summer temperatures, by exact timing of the duration of soaking, and by the use of soaking agents. However, the influence of bacteria escapes control because one must keep in mind that a sufficient softening of the collagen fiber is or might be slower than the effect of bacteria on the danger zone in the papillar layer I just mentioned. This is particularly important for temperatures which sometimes, as in the summer, rise above 20°C. It cannot be determined which role may be played by the unknown history of the raw stock.

A loose grain on vachette leather is without doubt helped along in the limes, particularly in old limes and in limes of higher temperature. What are the true causes, whether they are in the first place of chemical nature or, as in old limes, connected with bacteria activity, or both, or whether the chemical effects are stronger after previous bacteria activities, is very difficult to say and even more difficult to grasp analytically. One thing is sure: short, new, strongly sharpened limes cause much less loose grain than old limes. Also, elevated temperature in the lime favors loose grain. On the other hand, one must consider that it is much more difficult to make a soft, uniformly colored vachette leather of good feel in a short, new, strongly sharpened lime compared to a slower acting mild lime. What I have said, and I must stress this point again and again, is valid particularly for our hard water.

We are of the opinion that the preliminary conditions for a loose grain on vachette leather are caused largely by the history of the raw stock and may lie in the soak or in the limes and that one of the main causes may be warm limes and old limes. We were unable to notice a marked improvement in tight grains by painting. In this procedure, the usual mixture of Na_2S – $Ca(OH)_2$ could act upon the grain side only for a short time; afterwards, the hides came into a straight lime for from one to five days. At all times, care was taken during these experiments to obtain a sufficient liming for vachette leather, i.e., a complete removal of hair, including fine hair and scud so that later there would be no difficulties in coloring the leather surface in straight aniline dyes.

The last step in the beamhouse which could be a cause of a loose grain is deliming and, even more so, bating. I leave out intermediate steps during which the white hides, after liming in vats and before further processing, are stored in water from which the temporary hardness has been removed and which must not be fresh. Included in these intermediate steps are scouring, sorting and splitting.

I believe that we have tested each and every possible variation of bating and deliming for their effectiveness, not only experimentally but also in regular runs in the beamhouse for a considerable length of time: bating and deliming, or vice versa, one after the other, or together, in vats, in drums, in paddles, at all temperatures, from one-half an hour to overnight treatment,

and with all materials for deliming and bating. I do not believe that deliming has any effect on loose grain but that bating certainly does. On some hide packs one can tell that not only an extended bating procedure (and naturally more so at elevated temperatures) but also a short bate influences the tightness of the grain. I stress particularly also too short a bate. By and large, however, the differences in tightness of grain in the numerous bating tests which we have conducted are surprisingly small.

One important question in the problem of loose grain, however, is this: How is it that the phenomenon of more or less loose grain may appear at irregular and sporadic intervals? Making sure of the existence of this leather defect is difficult, because during the course of manufacturing every day several hundred vachette hides there will always be one or another lot of leather with more pronounced loose grain. The following lots again will be normal. Nevertheless, there are without doubt periods during which loose grain presents a striking general appearance so that the question arises for the vachette production: Where are the real causes to be found? As yet, we are unable to answer this question to our complete satisfaction. The answer is difficult or even impossible because of the unknown history of the raw stock.

How to overcome in the plant such a phenomenon on the grain of vachette leather, which materials may be used in the other departments of the plant, such as in tanning and finishing, and furthermore what other causes of loose grain may exist in the other sections of the tannery, all these lie beyond the framework of our present discussion.

CLEANLINESS OF GRAIN

As far as cleanliness of the grain for strictly aniline-dyed leather is concerned, the liming which favors loose grain is a necessity: liming to the extent of removing from the grain all substances which can disturb the coloring later on, and this means thorough liming and thorough soaking and bating. Twenty or 25 years ago, this problem of coloring vachette or strap leather was even more important than nowadays. In the meantime, the technique of finishing leather has acquired methods of making good, saleable, colored vachette leather from stock of less immaculate surface, whether as in the U.S.A., with the help of the corrected grain (the simplest method to solve certain problems quite radically), or with pigment finishes of all shades which help to make defects of the hide or impurities of the grain invisible. If one attempts to color vachette leather strictly with aniline dyes, it is essential that the leather be free of mechanical hide defects, and after coloring it must show a completely uniform surface, i.e., it must be possible to color the leather surface with straight aniline dyes absolutely uniform in shade, without shadows and clouds, without undertone, without darker and lighter spots.

It must be a leather with that peculiar "brilliance" which cannot be produced at all or only approximately by other finishing methods.

From the point of view of raw stock, the number of vachette sides which are suited for strictly aniline dyeing is already very limited because, as you know, immaculate hides are much less frequent than hides with grain damage. By embossing artificial grains, the number of hides suited for strictly aniline dyeing can be increased. But it is a fact that in Germany and in other European countries the smooth aniline leather still takes first place in the novelty trade, i.e., it pays highest prices.

At this point, the question becomes interesting as to which properties are required for the surface of cattle hides selected for such leather, i.e., properties which must be acquired first in the beamhouse so that after tanning the leather can be colored without difficulty by strictly aniline dyes. One may pose the question also this way: What can or must be done in the beamhouse in order to produce a white hide which can be tanned and fatliquored in such fashion that the surface of the leather in the vegetable-tanned and fatliquored condition appears perfectly uniform to produce, after strictly aniline dyeing, a perfectly uniform color shade and still not show a loose grain?

To obtain for the novelty trade leathers with an optimum of clean grains with respect to coloring, the same degree of cleanliness is necessary on the white hide. Very thorough liming is the first condition; hair, fine hair, and scud must be completely eliminated. Scudding—formerly we did not shy away from handgraining all stock in the white—becomes a very important procedure, and in this connection especially, the loosening of the scud mainly in the flanks and in the neck. I want only to mention that there was a good deal of experimenting when best to scud, whether out of warm water after liming, or after deliming, or after a kind of preliminary bate, or after bating.

In making white hides with grains clean for coloring, an important part naturally is played by deliming, i.e., elimination of the combined and capillary-absorbed lime to such an extent that the white hide becomes free of lime. Let us make a little detour into tanning chemistry; deliming is a rivalry—I use a word from Stather's book "*Gerbereichemie und Gerbereitechnologie*" (*Tanning Chemistry and Tannery Technology*) between the acid components of the collagen combined with the lime (Stather calls them "collagen acid") and the deliming acids. The dissociation constant of collagen according to Küntzel and Biederman is $2 \cdot 10^{-6}$. Accordingly, only deliming acids with dissociation constants above this value can or could eliminate the combined lime from the white hide. These constants cannot be ascertained readily for all deliming materials. The capillary-absorbed lime, however, can be washed out of the white hide by using carbonate-free water. Should there be any lime blast, the initial pH of the float must show a definite minimum value.

At this point I would like to point out the effects of the "specific factor" in our plant inasmuch as it is caused by tannery water. After elimination of

its temporary hardness, the water is used for deliming and bating with a permanent hardness of 430 ppm. What are the effects of such hardness in the processes? Maybe one should even look further back: What was the effect of this water whose hardness was already in the limes? Surely one can ponder all possibilities of reactions and formulate what takes place in a lime, i.e., in an old Na_2S - $Ca(OH)_2$ lime. Whether those analytically tangible proceedings in a lime also conform, however, with our rules in the presence of fatty acids and other fat- and albumen-decomposition products of all degrees, is not altogether a certainty to me. What part, for instance, is played in a lime by lime-fatty acid combinations which might originate in the natural grease?

In examining the surface of a pack of leather (after it has been completely delimed in the white and finished up to the point of coloring, including fatliquoring and glazing, etc.) it appears at first glance uniform and clean. No dark spots, no lime tannate stains and no lime blast are visible. If we show such a pack in this condition, for instance, to the members of an institute on an inspection visit we hear quite frequently the question: What was done to bleach these leathers so beautifully and uniformly?

We ourselves, however, see on part of these leathers quite different features. We notice very fine, dark, irregular stripes which look like an entanglement of hardly visible lines and which are noticed by an outsider of the plant only if they are especially pointed out. When the leather is then colored with aniline dyes, one can see on some packs that these irregular delineations appear more pronounced, and that on other packs they are less visible or disappear altogether. If the tannage is conducted with specific tanning materials, or if a certain pretannage is inserted, one will notice that the leather, in the off-board stage, no longer shows these delineations or clouds. But after coloring they re-appear in a more pronounced degree.

Our question—and we have tried to find an answer in uncounted experiments on almost 10,000 hides—is this: Where and how do these remarkable cloudy delineations originate which appear more pronounced after tanning and coloring in one case, and which in another case disappear? The experiments, through which we investigated and collected all factors we could think of, resulted in some instances in a reduction of these cloudy figures to the borderline of visibility but never did they disappear completely. Naturally, we have long since found ways and means in other departments to assist in eliminating this phenomenon. But we would like to determine its real cause. If such packs are handed over to one of the numerous coloring or finishing experts, the less experienced will promise an immediate remedy, but the experienced are more cautious in judging the possibilities of remedies. The result is quite consistently the same: never is this phenomenon eliminated completely. But this is probably not a problem of coloring as much as a beamhouse problem or a combination of various factors.

CONCLUSION

I shall summarize my speech in a few sentences:

For a vachette leather plant of our structure and with our production program the following basic principles present themselves in the beamhouse:

1. Soak and limes must be directed towards the main product, i. e., vachette leathers for the novelty trade, a leather of typical feel and firmness. In doing so, the most difficult problem is to stay along that middle line which fulfills best the requirements of a tight grain on one side and impeccable cleanliness of the grain, that is thorough liming, on the other side. These two problems are like two areas with the road like a narrow mountain path between them. One has to take great care not to step off too far to the right or to the left.

2. To make vachette leather for the upholstery industry one may insert an after-liming to obtain leather with a cloth-like feel, in particular since loose grain on this item does not play as important a role as on portfolio leather.

3. The firmness of the numerous other types of leather, as well as of the various splits, has to be regulated by other means in tanning and finishing.

4. Of all the beamhouse procedures which can influence the character of leather, the bate is one of the most reliable ones. The bate is easiest to adjust to the individual type of leather.

5. The "specific factor" of the plant which we have discussed in detail leaves its imprint on all procedures in the beamhouse. This "specific factor" has its strongest effect on account of the variety of the production program with its demand all at the same time for diametrically different leathers.

6. The almost unknown history of the raw stock influences the efficiency of the beamhouse in an uncontrollable way.

My presentation has been from the practical end which, so far, has not raised many voices in this circle. I have said very little about tannery chemical problems because it is not greatly concerned with what I wanted to discuss with you. Some 28 years ago, the former director of the Kaiser Wilhelm Institute for Leather Research, Professor Bergmann, was visiting our beamhouse. When I asked him how one could explain a certain phenomenon on a white hide of which I showed him a section, he looked at me for a long time with his big black eyes and finally replied: "Perhaps fifty years from now, tanning chemistry might begin to formulate an answer." Well, 28 years of this half-century have elapsed in the meantime.

I would like to close with this statement: To solve so many problems which appear to lie almost exclusively in the practical end, the co-operation of the leather chemist is indispensable. Because it is the leather chemist who can

and will lead the judgment of the practical man from the uncertain realm of experience into the domain of secure comprehension. However, a great deal of patience is needed with regard to the problems we have discussed here because it is by no means certain that Professor Bergmann's 50 years will be sufficient to produce explanations satisfactory to the leather chemist.

There are three roadblocks to scientific advance, all of which reflect misapprehensions about the true nature of science and technology. The first is an overemphasis on the numbers game — the notion that scientific strength can be augmented simply by multiplying the number of scientists. Actually, the progress of our society depends less upon numbers and more upon an advancing quality of professional accomplishments.

Our dynamic society anticipates and requires new jobs, an upgrading of old jobs, a still higher standard of living, better health and stronger defense. The fulfillment of these needs requires a new order of excellence and creativity in the nation's professional work. Today we have a greater shortage of basically educated, versatile young talent than of numbers of scientists and engineers.

—From an address by Dr. J. R. Killian, Jr., President, Massachusetts Institute of Technology.

CHEMIST A NECESSITY

Tanners may claim that they cannot afford to employ chemists. For my part, I am decidedly of the opinion that they cannot afford not to employ a chemist. If a tanner has only a small place, he should arrange with other tanners in his neighborhood to cooperate; between them the expense would be very moderate. It certainly would be a good deal cheaper to pay a fair price for steady services from a chemist than keep losing 10% on the value of your bark. Figure up your bark costs for one year and see what 10% of it amounts to. Bark tanners may laugh and think that this talk is all foolishness. All right; at the same time let them have the spent bark from each leach analyzed daily for from two to four weeks. They may find enough irregularities in leaching to make them turn blue and red. . . . . I do not suppose that my advice will have any influence on the minds of many lazy tanners who seem blind to what science can do for them, but possibly here and there some earnest and ambitious man with a small tannery may try and get other tanners to join with him in hiring a chemist, experimentally, so to speak, for six or twelve months. Such tanners, instead of encouraging their chemist to work on fancy schemes of quick tannage, should begin by keeping him busy on watching their spent tan and analyzing the currying and finishing materials they use. . . . . I know that it is going to cost tanners some money to have their spent tan from each leach carefully analyzed, but it will be found that such cautiousness will be handsomely repaid; and, once followed, will never be dropped.

—*Modern American Tanning*, Vol. II (1910).

Some Notes On Metallic Stains On Leather

J. Jacobs Tancous and Fred O'Flaherty

Department of Basic Science in Tanning Research
Tanners' Council Research Laboratory
University of Cincinnati
Cincinnati, Ohio

It is well known that the presence of iron in a vegetable tanning process makes ink-like stains on the leather, but many other stains caused by metallic elements are seldom recognized. Metallic stains can be caused at many stages in handling of skins and hides and may not become apparent until some later process causes a chemical reaction with the metal.

MERCURY STAINS

In the days when bichloride of mercury was the agent used in treating restricted hides, it was very difficult to make white or light pastel shades from such hides. When they were unhaired in lime-sulfide solutions, the mercury reacted with the sulfide to form a mercuric sulfide and a smoky-colored grain resulted. The reaction that occurred is represented by the equation shown below.

$$HgCl_2 + Na_2S \rightarrow HgS + 2\ NaCl$$

The use of bichloride of mercury was soon forgotten after the Tanners' Council Research Laboratory developed the new disinfecting method for treating restricted hides. This method is the use of sodium acid fluoride 1: 10,000 concentration.

LEAD STAINS

Lead salts have been found to cause stains in green salted hides which had unknowingly been put in a freight car in which batteries had been shipped. This could happen if scrap lead or some colorless lead salt had been in the car and it was not cleaned out. The equation shown below represents the reaction that occurs when hides contaminated with lead are subjected to the lime-sulfide solution. In such cases we find that the black lead sulfide stains

$$Pb^{++} + Na_2S \rightarrow PbS + 2\ Na^+$$

are only on that part of the hide which came in contact with the lead. In bundled hides we have seen the stain only in the exposed area of the hide.

OTHER METALLIC STAINS

During the past year we have had many samples of salt brought to our attention. These salts were collected from hides which turned black in the

lime liquors. Analyzing the salt collected from such hides, we found small dark stones intimately mixed with the sodium chloride cyrstals. A solution made by heating these dark stones in hydrochloric acid and added to an alkaline sulfide solution gave a dark precipitate of metallic sulfide. These stones were subjected to analysis by a spectrograph; the analysis showed much iron to be present and other metals such as tin and lead were also found. Iron, tin and lead all produce dark sulfides as shown below.

$$2\ Fe^{+++} + 3\ Na_2S \rightarrow Fe_2S_3 + 6\ Na^+$$
$$Sn^{++} + Na_2S \rightarrow SnS + 2\ Na^+$$
$$Pb^{++} + Na_2S \rightarrow PbS + 2\ Na^+$$

IDENTIFICATION OF STAINS

The identification of stains on hides or leathers is best done with a spectrograph or a spectranal; it can be done by spot testing but not with dependable accuracy. The areas stained are cut out and incinerated to the inorganic ash. This ash is then dissolved in concentrated hydrochloric acid for testing. A preliminary test is performed to see if the stain is metallic or organic in nature. If a few drops of the hydrochloric acid solution give a black precipitate in a solution of ammonium hydroxide containing sodium sulfide, the stain probably is due to some inorganic metal element such as bismuth, mercury, tin, iron, copper, silver, nickel, cobalt or lead. If, however, a black precipitate does not form, the stain probably due to some organic defect such as filth stains, gelation, etc.

A quick test for spotting the metal involved is to form the hydroxide or oxide by adding several pellets of sodium hydroxide to the test solution in a spot plate. A white precipitate going to yellow indicates bismuth; intense yellow—mercury; white going to gray—tin; red brown—iron; blue—copper; white—silver; green—nickel; blue going to pink and then to dark brown—cobalt; white going to red orange—lead. These colors develop with the higher valence states of the elements, so to be sure that the element is in its higher valence state, a second test should be run in which an oxidizing agent is added before the sodium hydroxide.

Another quick identification involves neutralizing the hydrochloric acid test solution with calcium hypochlorite. This must be done in a hood because of the evolution of chlorine. The same precipitates form as with the sodium hydroxide except that nickel forms a black precipitate and lead forms a dark brown precipitate. The white precipitates that form with mercury and silver later dissolve.

After the preliminary testing, spot tests are used for further identification of the metal element. The reagents found useful for the identification of iron are orthophenanthroline, potassium thiocyanate or potassium ferrocyanide; of tin, phosphomolybdic acid and methylene blue; and of lead, benzidine,

tetramethyl-diamino-diphenyl-methane or gallocyanine. These methods of spot testing and many others are given in *Cations* by G. Charlot, D. Bezier, and R. Gauguin, (Chemical Publishing Co., 1954) and *Spot Tests* by F. Feigl, (Elsevier Publishing Co., 1946).

As mentioned above, the more precise method of identifying stains due to metallic elements is the use of a spectrograph or a spectranal. The spectrograph is more accurate but is an expensive piece of equipment not available in most laboratories. The spectrograph method involves exciting the sample, preferably dry, in an arc and taking a photograph of the spectrum produced. The excitation lines are thus recorded and are later identified. Each cationic element has its own spectral lines, so identification of the lines allows for the determination of the cations present in the sample.

The spectranal is a very useful instrument for identifying cations. Although it is not as elaborate as the spectrograph, it is simple to use and is much superior to spot testing for the identification of cations. For analysis with a spectranal, the sample must be soluble in a 10% nitric acid solution. If it is not soluble, it is dissolved in aqua regia, taken to dryness and redissolved in 10% nitric acid. If the sample is organic, it is incinerated to the inorganic ash before being dissolved in aqua regia, taken to dryness and redissolved in a 10% nitric acid solution. The test solution is placed in the spectranal and excited by current; excitation occurs at a platinum electrode and is studied with a spectroscope. The spectral lines are read and identified to find the cations present in the solution.

STAIN PREVENTION AND REMOVAL AT THE TANNERY

The hides or skins, if known to be contaminated with heavy metallic salts, could be processed without stains if sodium sulfide (or other sulfide) is avoided in the lime unhairing liquor*. It is the sulfide that causes the severe staining, immediately turning these heavy metallic elements black. Once the black sulfide is formed, it is difficult to remove with the usual process of making leather. However, if a hydrochloric acid pickle is used instead of the customary sulfuric acid pickle such sulfide stains as are caused by lead and iron can be reduced. Treating stained hides in a 5% hydrochloric acid pickle for 24 hours has been effective; however, some sulfides are responsive to a permanganate-oxalic acid bleach rather than to the hydrochloric acid.

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*However, chocolate-brown stains due to lead have been observed in one tannery on limed stock, even though no sulfide was added to the lime liquor. Presumably enough sulfide to form the black PbS was produced in the lime liquor by breakdown of epidermal keratins.

Report of the Subcommittee for Investigation of Methods for Detection and Estimation of Lignosulfonates In Vegetable Tannin Blends

J. JANY, *Chairman*

INTRODUCTION

This subcommittee was established at the meeting of the Tannin Analysis Committee in Cincinnati, on June 7th, 1953, in order to investigate analytical methods for the qualitative detection and quantitative estimation of lignosulfonates. The following members participated: R. E. Barnwell, M. Baum, S. Dahl, J. M. Hinkle, J. Jany (*Chairman*), V. R. Power, L. Rayfield (*Assistant Chairman*), and J. W. Wolfe.

The Subcommittee decided to restrict its investigation to straight commercial lignosulfonate preparations and their blends with vegetable extracts, and not try to pay any attention to possible interference of syntans. Since syntans are more expensive than vegetable extracts, the possibility of their use as adulterants is very small; hence, they may not interfere with the analysis too often. Besides, the possibilities of syntan interference are most various and complicated because of their different chemical characters, and the members of this subcommittee had no time and opportunity for such extensive investigations. This part of the problem was left to future committees as a long-term proposition.

In carrying out its investigations, the Subcommittee used the following procedure:

Samples were made up by J. Jany from commercial lignosulfonate preparations and vegetable-extract blends. Two series of samples were submitted to the members. Samples 2, 3, 4 and 5 of First Series (Table I) contained different vegetable extracts in order to check the influence of individual extracts upon the reactions. Identical samples were submitted to all members for investigation. Low-sulfited quebracho, chestnut, wattle, and high-sulfited quebracho were tested for their interference in the first series, and after it could be stated that lignosulfonates can be detected in the presence of any of them, the blends of the second series were made up of equal parts of wattle, chestnut, and high-sulfited quebracho.

The first series contained Lignosol TS (ammonium salt of lignosulfonic acid), the second series Lactanx (a preparation of high acidity) in neutralized form. Besides these two series investigated by every member, a special series, "1A", was made for M. Baum alone, containing neutralized Lactanx as lignosulfonate and a 1:4 blend of chestnut and high-sulfited quebracho.

Compositions of all samples are described in Table I, whose headings need the following comments:

The name "Spruce" is used for commercial preparations containing lignosulfonic acid and its derivatives.

"Spruce Content in Liquids" means grams of lignosulfonic acid preparation contained in 100 grams of the liquid sample.

"Spruce Content in Solids" means grams of solid residue of liquid lignosulfonic acid preparation contained in 100 grams of solid residue of the liquid samples.

TABLE I

COMPOSITION OF SAMPLES

Sample No.	First Series		1A Series		Second Series	
	Spruce Content in Liquids	Spruce Content in Solids	Spruce Content in Liquids	Spruce Content in Solids	Spruce Content in Liquids	Spruce Content in Solids
L	——	——	——	——	100.00%	100.00%
V	——	——	——	——	0.00%	0.00%
1	100.00%	100.00%	100.00%	100.00%	3.22%	2.98%
2	4.93%	5.81%	10.45%	9.62%	15.82%	14.75%
3	70.88%	74.33%	2.08%	1.91%	0.00%	0.00%
4	0.00%	0.00%	45.45%	43.18%	38.12%	36.20%
5	16.96%	21.63%	6.79%	6.20%	8.44%	7.82%

All investigators knew that Sample 1 of First and 1A Series and Sample L of Second Series consisted of straight lignosulfonic acid preparation, and that Sample V of Second Series contained straight vegetable blend. Their task was to detect and to determine lignosulfonic acid in the unknown samples. Their results were compared with the true composition in order to judge the reliability of the method.

Many members have also examined blends of their own make in order to test the interference of certain substances.

The members of this Subcommittee tried to collect all references available from the literature and tested most of the previously published methods experimentally. References considered useful for our purposes are listed below, but since the literature on this subject is quite extensive, the list may not be complete; thus, some possibly effective methods may have been left untried.

Our purpose was partially qualitative detection and partially quantitative estimation; therefore, this report consists of two parts: qualitative tests and quantitative tests.

QUALITATIVE TESTS

Tingle's Color Reaction (1) was investigated by S. Dahl and J. Jany. It was found that the coloration is not characteristic and can be ob-

served just as well in the absence of lignosulfonates. Therefore, this method has to be rejected as entirely unsuitable for detection of lignosulfonates.

Determination of Methoxyl Groups, according to Zeisel (7). This method will be discussed in the quantitative part, but it must be mentioned here that the presence of methoxy groups is no proof of the presence of lignosulfonates because straight vegetable extracts also yield considerable methoxyl.

Van der Hoeven's Color Reaction (2), being based upon the detection of methoxyl, has to be rejected for the same reason as above. Besides, it appears to be somewhat awkward and cumbersome.

Grasser's Vanillin Reaction (3) was investigated by J. M. Hinkle and L. Rayfield. The former met difficulties when separating the ether layer from the water solution and, even after he was able to overcome this difficulty, he found results exactly the opposite of Grasser's: the coloration of the ether layer was paler in the presence of increasing amounts of lignosulfonates, both before and after the addition of phloroglucinol. L. Rayfield found the method unserviceable too; thus it must be discarded.

Kilchner's Chromatographic Method (4) was investigated by J. M. Hinkle, R. E. Barnwell, and L. Rayfield. This method is based upon chromatographic absorption of tanning materials and lignosulfonates by filter paper and observation of their fluorescence in ultraviolet light of 3660 A. wave length. Lignosulfonates show blue fluorescence and can be easily recognized by a peculiar wavy edge of the chromatogram.

L. Rayfield's experiences were generally favorable, although he met some difficulties in recognizing the composition of the samples. R. E. Barnwell came to the conclusion that the method is far from being certain enough in its present form. The most extensive investigations were made by J. M. Hinkle, who found the reaction extremely sharp when using pure lignosulfonate solutions and had favorable experience with some blends of his own, but was disappointed when applying it to the samples supplied by J. Jany. The main difficulty was that lignosulfonates changed the diffusion characteristics of extracts and there was no clean separation. According to H. Martin (5) similar difficulties arise when using alumina columns instead of paper.

J. M. Hinkle also tried to apply ultraviolet light of shorter wave length (2537 A.) without achieving considerable improvement.

In the Subcommittee's opinion the method cannot be considered certain enough in its present form, but further investigations may succeed in making it suitable for qualitative detection or even for quantitative estimation. The method is recommended for further study.

The Reaction of Procter and Hirst (6) was investigated in its original form by S. Dahl, J. Jany, and L. Rayfield. The reaction is too sensitive and

sometimes entirely misleading. Especially disturbing are precipitates formed by pure vegetable extracts in the presence of hydrochloric acid. Therefore, the Subcommittee does not consider this reaction as suitable for the detection of lignosulfonates.

The Cinchonine Reaction (11) was subjected to careful investigation which will be reported in the quantitative part with a description of the method. In most cases the presence of lignosulfonates was indicated with safety, but weakly positive reactions were sometimes found in their absence. The amounts found were very low, and have but little bearing upon the reaction's reliability as a quantitative method; still, it leaves some doubts about its safety as a qualitative test.

Since Gerngross' reaction (see below) indicated the presence of lignosulfonates in all cases safely, the Subcommittee does not believe that the cinchonine reaction should be used exclusively for detection of lignosulfonates. However, it is recommended as a confirmative test and as a method for quantitative estimation.

Gerngross' Modification of the Procter-Hirst Reaction (22) was examined by S. Dahl, J. M. Hinkle, J. Jany, and L. Rayfield. In order to avoid errors caused by decayed wood and by precipitation of extracts by hydrochloric acid, O. Gerngross first clarified the analytical solution with hydrochloric acid and then carried out the reaction on the clear filtrate. According to the references, the above errors could be safely eliminated in this way, but the sensitivity of the reaction was lessened too far and very small amounts could not be detected.

Our investigators eliminated this trouble by raising the concentration of the analytical solution and by changing the time of observation. Instead of the originally suggested solutions of 0.4% tannin content, solutions containing 25 grams per liter of liquid blend, or 12.5 grams of solid extract, were used, and observations were made after 2 minutes and after 15 minutes, instead of after 15 minutes only. In doubtful cases, when very small amounts of spruce were present, another solution was made up whose strength was three times higher, and which was clarified with three times the amount of hydrochloric acid.

The following procedure was adopted for these investigations: Dissolve 25 grams of liquid, or 12.5 grams of solid extract in hot water, and make up to 1000 ml. Filter through Whatman No. 41H or similar rapid paper, put 200 ml. of the filtrate into a 250-ml. beaker, agitate with 4 ml. conc. hydrochloric acid, and let stand for 15 minutes. Mix about ¼ part of the liquid with Celite (Johns Manville), or similar filter aid, and filter through Whatman No. 42, or similar fine paper, and Buchner funnel, using suction. Discard the filtrate and filter the rest of the solution through the impregnated paper. Use this second filtrate for the test.

Mix 10 ml. of the filtrate with 1 ml. aniline in a test tube, add 4 ml. conc. hydrochloric acid, shake well, and let stand. Observe for cloudiness after 2 minutes; and 15 minutes.

INTERPRETATION OF READINGS

Precipitate in either 2 or 15 minutes: positive, absolutely certain.

Appreciable cloudiness in 2 minutes, heavy in 15 minutes: same as above.

Hardly appreciable cloudiness in 2 minutes, somewhat heavier in 15 minutes: doubtful, needs confirmation.

Clear in 2 minutes, clear or very slight cloudiness in 15 minutes: negative.

For confirmation, if needed, dissolve 75 grams of the liquid extract and make to 1 liter. Mix 200 ml. of the solution with 12 ml. conc. hydrochloric acid and proceed as above. The cinchonine reaction can also be used as confirmation.

All reports sent by the investigators showed good concordance.

Notes: S. Dahl proved that old, dark-colored aniline is just as efficient as the freshly distilled. The formation of precipitate is aided by the presence of vegetable tanning materials, and it appears heavier in blends containing high amounts of lignosulfonates than in straight lignosulfonate solutions. However, there is no need to add tannin to the solution because straight spruce preparations contain lignosulfonates in such high concentrations that precipitates are formed under any conditions. If leather extracts, with very low solid contents, have to be investigated, 2 ml. of 1.5% tannic acid solution —as described for the cinchonine reaction—should be added to the test tube.

The Subcommittee does not believe that any further investigation of the method would yield appreciable improvements and considers it safe enough in its present form. However, the Subcommittee feels that Barnwell's reaction (see below) has definite advantages, and might eventually replace it. The Subcommittee also hopes that the chromatographic method can be made more reliable. Therefore, the Subcommittee recommends Gerngross' reaction for provisional adoption, its final official adoption depending upon the results of future investigations of the other two methods.

Barnwell's Reaction was introduced by R. E. Barnwell and investigated by S. Dahl, J. M. Hinkle, and L. Rayfield. Some references were found in the literature about the formation of precipitates between lignosulfonates and beta-naphthylamine in hydrochloric acid solution (23, 24, 25) and Barnwell applied this reaction for qualitative detection, as follows:

Beta-naphthylamine hydrochloride solution: Prepare 1000 ml. of approximately 0.3*N* hydrochloric acid solution by diluting 25 ml. conc. acid to one liter. Dissolve 30 grams of beta-naphthylamine in this solution by heating, cool, filter, and re-adjust to 1000 ml. Store in a dark-colored, glass-stoppered bottle.

Qualitative Test: Dissolve 5 grams of liquid extract in a 150-ml. beaker, adjust the volume to 50 ml. with distilled water, add 1 ml. of conc. hydrochloric acid, and mix thoroughly. Transfer to a 100-ml. graduated cylinder, fill up to 100 ml., shake well, and allow to settle overnight. Take 20–25 ml. of the clear liquid, dilute to 100 ml., and mix well. Fill a test tube half-full with the clear, diluted liquid, add 5 ml. of beta-naphthylamine solution, shake well, and observe for precipitate. Formation of a precipitate or cloudiness indicates the presence of lignosulfonates.

R. E. Barnwell tested all samples of Series 1 and 2 by this method, and obtained the following results:

Series 1: Sample 1, heavy precipitate; 2, cloudy; 3, heavy precipitate; 4, clear; 5, medium precipitate.

Series 2: L, heavy precipitate; V, clear; 1, slight turbidity; 2, cloudy or light precipitate; 3, clear; 4, medium precipitate; 5, slight turbidity.

This is in very good accord with the true composition, but the other investigators met some difficulties in applying the method. The main trouble was that most of them found a positive reaction for sample 3 (series2) which contained no lignosulfonate. Most investigators extended the observation period to one hour or even to 24 hours, which was definitely too long. In order to make the method serviceable, the most favorable observation period has to be found experimentally and specified definitely. Barnwell mentions that results can be easily observed after one hour, because in this time cloudiness will turn into flocculation, but it seems very probable that even this time is too long and that it would be safer to check for cloudiness after a few minutes, even if the precipitate is not as well formed at that time. The effect of temperature should also be investigated to see if it has any influence upon the results. Probably the second dilution should also be altered according to the quantity of lignosulfonate present. Barnwell diluted all solutions 4–5 times. This may be all right for high lignosulfonate contents but perhaps for low ones a 1:1 dilution or no dilution at all would be preferable.

The molecular weight of beta-naphthylamine being higher than aniline, it seems logical to expect that heavier precipitates will be formed, which can be observed more easily. Clarification of the solution with such large amounts of hydrochloric acid should increase the safety of the reaction by eliminating all substances which might cause misleading precipitates in acid solutions. Therefore, the Subcommittee recommends the method for further study.

Other Methods. Descriptions of several methods can be found in the literature, particularly in Bergmann's "Handbuch" (21). A paper by Gustavson in the publication of the Royal Swedish Insitute for Engineering Research (26) refers to Swedish investigations into various precipitating agents, and mentions that most promising tests were made with 4,

4-bis-dimethylamino-diphenylmethane. This latter reagent was not available to our members and most of the other methods did not seem worth investigating.

QUANTITATIVE TESTS

Determination of Methoxyl Content. This method was investigated by M. Baum and S. Dahl. It was considered the safest way to estimate the amount of lignosulfonates because, according to Zeisel (7), methoxyl groups can be converted into methyl iodide quantitatively, and the iodine content of the latter can be determined either gravimetrically as silver iodide (8) or, according to Vieböck (9), volumetrically, by oxidizing it to iodic acid (10).

A great number of different reagents and apparatuses were recommended by various authors for this purpose; our investigators decided on the following:

Apparatus: Made to specifications furnished by the Marathon Corporation, Rothchild, Wisconsin, and available from H. S. Martin and Company, Chicago, Illinois.
(See Figure 1.)

Reagents:

Hydriodic acid, reagent grade, spec. gr. 1.70.
Phenol, reagent grade.
Red phosphorus, C. P.
Cadmium sulfate, 10% aqueous solution.
Sodium thiosulfate, 10% aqueous solution.
Sodium thiosulfate, 0.05 *N* solution.
Sodium acetate, 10% solution in glacial acetic acid.
Sodium acetate, 25% aqueous solution.
Bromine, reagent grade.
Carbon dioxide, in cylinder.
Sulfuric acid, approximately 1 *N* solution.
Potassium iodide, freshly prepared 10% aqueous solution.
Formic acid, spec. gr. 1.2.

Sample: (*a*) *Dry Solids*: Thoroughly pulverized and mixed residue from determination of moisture by drying to constant weight at 105°C.

(*b*) *Solution of liquid extracts*: In case moisture is not determined, it may be more convenient to use as the sample 1 ml. of a solution of the liquid extract prepared by dissolving 50 grams (exactly weighed) in 1 liter of warm water and making to volume after cooling. The sample weight (mg.) contained in 1 ml. equals the number of grams of extract per liter.

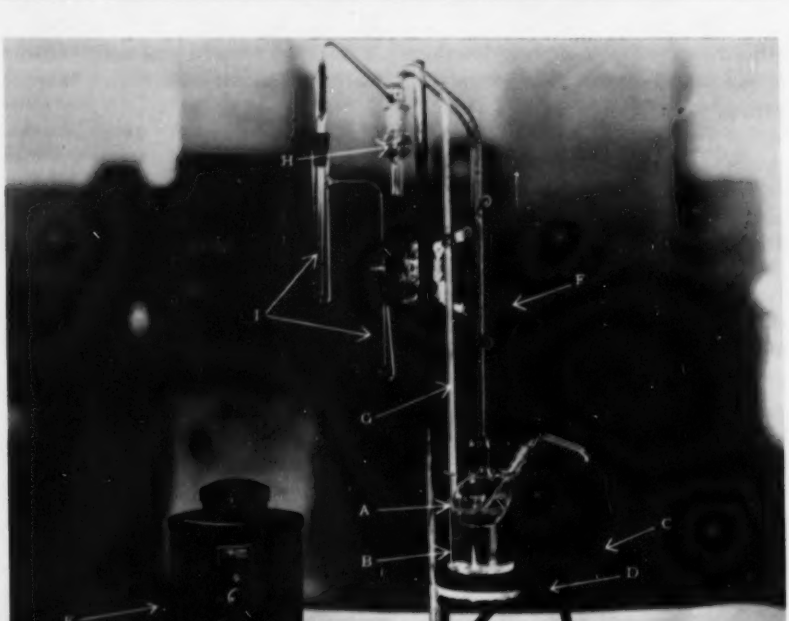

FIGURE 1.—Apparatus for determination of methoxyle content. A, digestion flask; B, glycerine bath; C, connection to CO_2 cylinder; D, hot plate; E, autotransformer for control of hot plate heating rate; F, air condenser; G, thermometer for reading temperature of glycerine bath; H, wash chamber; I, absorption tubes.

Procedure: Charge the wash chamber (H) of the apparatus with 0.8 ml. of each of the 10% solutions of cadmium sulfate and sodium thiosulfate. If an apparatus other than the one referred to is used, the wash chamber capacity may also be different. In that case, use sufficient (equal) volumes of the two solutions to bring the liquid surface about 4 mm. above the tip of the inlet tube. Place 5 ml. of hydriodic acid, 2 ml. of melted phenol, and 0.2 to 0.4 gram of red phosphorus in the digestion flask (A) equipped with the air condenser (F). Removal of the side inlet armof the digestion flask permits introduction of the reagents. Replace side inlet arm and join it to the carbon dioxide cylinder connection (C). Pass a slow stream of CO_2 through the apparatus. Heat the digestion flask in the glycerine bath (B) to 135°–140° C. and run CO_2 through the system for 10 minutes after the above temperature is

reached. Then connect absorption tubes (I), each of which contain 10 ml. of the 10% solution of sodium acetate in glacial acetic acid and 12–15 drops of liquid bromine. Weigh to 0.1 mg. accuracy 40–60 mg. of the solid sample [see (a) under "Sample"] on a tared cigarette paper. Carefully fold the sample in the paper and place it in the digestion flask (A). The apparatus mentioned above is equipped with a ground-glass connection for removal of the side arm, thus permitting introduction of the sample and reagents. In apparatus not equipped with this feature the condenser has to be disconnected from the digestion flask. In that case, it is advisable to first run off the heat and let the digestion mixture cool somewhat before introducing the sample. If a solution of liquid extract is used as sample [see (*b*) under "Sample"], add the 1 ml. aliquot directly into the digestion flask from the pipet. Heat at 135°–140°C. with a slow stream of CO_2 bubbling through the system for at least 45 minutes. Then wash the contents of the absorption tubes with water into a 250 ml. Erlenmeyer flask equipped with a glass stopper and containing 5 ml. of the 25% aqueous solution of sodium acetate. Destroy the excess bromine in the flask by dropping formic acid into the solution and swirling until the bromine color disappears. Then add 10 drops more, stopper the flask and invert briefly so that any bromine in the upper parts of the flask is washed off. Add 10 ml. of the dilute sulfuric acid and 10 ml. of the 10% potassium iodide solution to the flask. Titrate the liberated iodine with the standard thiosulfate solution to a starch endpoint. A total of four determinations may be made with each charge of reagents in the digestion flask if solid samples are used. When liquid extract solutions are used as samples, new reagents must be added for each determination. The wash chamber solution should be changed whenever solid sulfur precipitates out. A blank should be run on the reagents and should be negligible. If not, longer preheating of the digestion charge may be necessary, or purification of the hydriodic acid. Such purification may be accomplished by heating the acid to gentle boiling for about two hours during which a slow stream of carbon dioxide is bubbled through it. When heating is stopped, the flow of gas should also be discontinued, as fuming acid is formed by passing the gas through at room temperature. The acid need not be colorless.

Calculation:

$$\% \text{ Methoxyl} = \frac{\text{ml. thiosulfate solution} \times \text{normality} \times 5.17 \times 100}{\text{Weight of sample in mg.}}$$

Report: Report the per cent methoxyl to the nearest 0.05%.

In the following test applications, the use of liquid samples is referred to as "wet method", the use of dry samples as "dry method".

All samples of Series 1 were investigated by both members, S. Dahl having applied both wet and dry methods. Series 1A and 2 were investigated by M. Baum alone, who applied the dry method exclusively.

The basis of evaluation of their findings was the methoxyl content they found in the straight lignosulfonate preparation. By multiplying this amount by the percentages in Table 1, the "theoretical methoxyl content" of each sample could be calculated, i. e., the amount of methoxyl which should have been found if the vegetable extracts were not interfering with the reactions. For example, S. Dahl found 7.60% methoxyl in Sample 1 of Series 1 (straight spruce); therefore, the theoretical methoxyl content of Sample 2 of the same series is calculated as : 5.81 x 0.076 =0.44%.

"Actual methoxyl content" is the amount actually found by the investigators. For example, S. Dahl found 1.70% in Sample 2.

"Deviation" is the difference between the two figures; in the example, 1.70 - 0.44 =1.26%.

When calculating the average deviation of one series, the deviations were summed up according to their numerical sizes, disregarding whether they were positive or negative, and the sum was divided by the number of tests. The numerical magnitude of deviation is not sufficiently characteristic because the same figure may be acceptable if the percentage of lignosulfonate is high but very erroneous if it is low. Therefore, the "relative deviation" was calculated as the quotient of deviation divided by theoretical methoxyl content, multiplied by 100. The average figure for relative deviations was calculated by dividing the numerical sum of deviations by the sum of theoretical methoxyl contents, and multiplying by 100.

Theoretical and practical methoxyl contents were in fairly good accordance in the presence of high amounts of spruce, but there were enormous discrepancies if the blend contained lesser amounts. This is understandable because straight vegetable extracts also yielded methoxyl percentages of considerable size, thereby introducing an error that increases with the ratio of vegetable tannin to spruce.

An attempt to eliminate this error was made by introducing "corrected values". These were calculated by multiplying the vegetable-extract content of the total solids by the natural methoxyl content found for that particular blend, and by subtracting the product from the actual methoxyl content. For example, Sample 5 of Series 1 contained 21.63 parts of lignosulfonate (Sample 1) and 78.37 parts of vegetable extract (Sample 4) in 100 parts total solids. Its theoretical methoxyl content calculates to 21.63 x 0.076 =1.64%. Actually 2.42% was found. Dahl found that the pure extract (Sample 4) contains 1.02% methoxyl, and, therefore, the error caused by 78.37% of this extract was 78.37 x 0.0102 = 0.80%. The corrected value calculates as 2.42 - 0.80 = 1.62%.

Deviations and relative deviations were calculated for corrected figures in the same way as for actual ones.

Naturally, no corrected values could be calculated for those samples whose actual methoxyl contents served as the base for corrections of other samples.

The results of methoxyl determinations are listed in Table II.
An explanation of the column headings follows:

First column	: Au and S	=Name of Author and Number of Series
Second "	: SNo	=Sample No.
Third "	: T.M.C.	=Theoretical Methoxyl Content, expressed in %
Fourth "	: M. %	=Methoxyl Percentage
Fifth "	: Dev.	=Deviation
Sixth "	: R. D.	=Relative Deviation
Seventh "	: M. %	=Methoxyl Percentage
Eighth "	: Dev.	=Deviation
Ninth "	: R. D.	=Relative Deviation

TABLE II
METHOXYL DETERMINATIONS

			Actual Values			Corrected Values		
Au&S	SNo	T.M.C.	M.%	Dev.	R. D.	M. %	Dev.	R.D.
Dahl	1	——	7.60	——	——	——	——	——
Dry	2	0.44	1.70	+1.26	+286.4	——	——	——
Method	3	5.64	5.57	−0.07	−1.3	5.22	−0.42	−7.4
No. 1	4	0.00	1.02	+1.02	∞	——	——	——
	5	1.64	2.42	+0.78	+47.6	1.62	−0.02	−1.2
			Av.	0.78	40.5	Av.	0.21	5.8
Dahl	1	——	4.28	——	——	——	——	——
Wet	2	0.21	0.92	+0.71	+338.1	——	——	——
Method	3	3.04	3.17	+0.13	−4.3	2.97	−0.07	−2.3
No. 1	4	0.00	0.50	+0.50	∞	——	——	——
			Av.	0.45	41.2			
Baum	1	——	7.46	——	——	——	——	——
No. 1	2	0.43	1.66	+1.23	+286.0	——	——	——
	3	5.54	5.96	+0.42	+7.6	5.63	+0.09	+1.6
	4	0.00	1.22	+1.22	∞	——	——	——
	5	1.60	2.48	+0.88	+55.0	1.53	−0.07	−4.4
			Av.	0.94	49.5	Av.	0.08	2.2
Baum	1	——	6.94	——	——	——	——	——
No. 1A	2	0.66	1.97	+1.31	+198.5	0.84	+0.18	+27.3
	3	0.12	1.35	+1.23	+1025.0	——	——	——
	4	3.00	3.85	+0.85	+28.3	3.14	+0.14	+4.7
	5	0.42	1.73	+1.31	+311.9	0.56	+0.14	+43.6
			Av.	1.17	111.9	Av.	0.15	11.3
Baum	L	——	7.42	——	——	——	——	——
No. 2	V	0.00	1.24	——	——	——	——	——
	1	0.22	1.41	+1.19	+540.9	0.21	−0.01	−4.5
	2	1.09	2.07	+0.98	+90.0	1.02	−0.07	−6.5
	3	0.00	1.33	+1.33	∞	0.09	+0.09	∞
	4	2.68	3.31	+0.63	+23.6	2.52	−0.18	−6.7
	5	0.58	1.71	+1.31	+194.8	0.57	−0.01	−1.7
			Av.	1.05	115.1		0.07	7.9

The following conclusions can be drawn from Table II:

(*a*). The reproducibility of results by different investigators seems to be satisfactory, although some small discrepancies can be noticed. According to the literature (10) the accuracy of the methoxyl determination is $\pm 0.1\%$ from the theoretical percentage, and assuming that the true value lies between Baum's and Dahl's actual methoxyl contents found in samples 2, 4, and 5 of Series 1, the agreement is good, because no difference above 0.2% can be noticed. Their figures for samples 1 and 3 of the same series differ by 0.32% and 0.40%, which proves either that they both had deviations larger than the permitted limit or that one author's figures were right and the other is rather far away from the truth. Although these discrepancies are rather small, it would seem advisable to investigate the method again and to try to establish better concordance between findings of different laboratories.

(*b*) The discrepancies might have been caused in part by the drying procedure which is unavoidable if dry substance has to be used. Tanning extracts and lignosulfonates suffer some kind of decomposition in drying which may affect their chemical behavior and also their analysis. The fact that the two investigators found different moisture contents in all samples seems to support this assumption.

Therefore, the application of the wet method seems to be of definite advantage, because in this way all discrepancies caused by drying can be eliminated. Besides, the weighing of small amounts of hygroscopic substance can be avoided. On the other hand, the water introduced by the wet method may cause trouble in the analysis, and, therefore, it has yet to be decided which method is to be preferred. Further investigations are needed for this purpose, because only a few tests of the wet method were done by Dahl.

(*c*). Samples No. 1 of both series 1 and 1A consisted of straight lignosulfonate products of different character. The composition of technical spruce preparations is subject to great variations; therefore, their methoxyl contents cannot be expected to be identical. Thus, Baum found 7.46% in the one, and 6.94% in the other. The real purpose of the procedure is to determine the percentage of spruce in blends; therefore, the methoxyl percentages have to be multiplied by a factor. According to the first finding, the conversion factor would be $\frac{100}{7.46}$ or 13.41; according to the second, $\frac{100}{6.94}$ or 14.41. Probably it will be necessary to establish factors for all known lignosulfonate products by determining their methoxyl contents in the pure state and to publish a list of these factors, so that the analyst may use them when examining tannery blends made with the addition of identifiable spruce preparations.

It will be far more difficult to analyze a commercial blend whose spruce component is not made known by the manufacturer. Of course, no individual factor can be applied in such a case because the analyst cannot know which

one to apply, and a general factor will be needed which can be used for all kinds of lignosulfonate preparations. It can be expected that a general factor may be established by taking the average value of individual ones and that this factor may come rather close to the truth in every case, if the spread between individual factors is not too large. However, this question has to be cleared up by careful investigation.

(*d*). The necessity of corrected values is quite evident, the interference of vegetable extracts being so large that the methoxyl actually found does not even give a clue to the real composition, except when the quantity of lignosulfonates is very large. In the case of the present investigations these corrections could be done easily and precisely, because both the composition of the blend and the natural methoxyl content of its vegetable component were well known.

This will never occur in practice where ready-made blends of unknown composition are laid before the analyst. All he obtains from the analysis is the actual methoxyl percentage, p, of the blend and, if he wants to calculate the percentage, X, of lignosulfonate products contained in it, he needs the following values:

p_1 = general methoxyl content of all lignosulfonate products,
p_e = average methoxyl content of the same type of vegetable extract, whose blend with lignosulfonate he has actually analyzed.

Then X can be calculated according to the equation:

$$p_1 \times p_e\ (100 - X) = 100\ p$$

Taking an Italian chestnut extract as a practical example, the analyst may find 2% methoxyl in it, i. e., $p = 2.0$. Then he has to know that lignosulfonates generally contain 7.0% methoxyl, i. e., $p_1 = 7.0$, and that the average methoxyl content of Italian chestnut is 1.4%, i. e., $p_e = 1.4$. Then according to the equation

$$7.0 \times 1.4\ (100 - X) = 200,$$

he will be able to calculate that his extract is actually adulterated with 10.7% lignosulfonate products.

The possibility of establishing a general methoxyl content p_1 for all lignosulfate products has been discussed already. The question is still open whether or not it will be possible to establish p_e values for all individual types of extracts which would be sufficiently constant and characteristic. In order to make this method workable, it is imperative to investigate this question thoroughly. If these investigations turn out successfully, a list of methoxyl contents of natural tannins must be issued in order to render the calculation of analyses feasible. As mentioned earlier, such a list of p_e values would be useful only where the nature of the admixed vegetable tannins is known.

(*e*) Generally, the accordance between theoretical and corrected methoxyl contents is quite satisfactory, but some discrepancies can be noticed in Series 1A which seem to need more investigation.

This conclusion can be drawn from these facts: Among all methods suggested for the purpose, the determination of methoxyl is by far the most precise, but it cannot be recommended for estimation of lignosulfonates in blends until all the investigations mentioned above are carried out to full satisfaction.

Precipitation with Cinchonine. This reaction was investigated by R. E. Barnwell and S. Dahl.

The method is based upon a publication of W. Appelius and R. Schmidt (11) according to which lignosulfonates form insoluble compounds with cinchonine in the presence of tannin and hydrochloric acid. The reaction has been examined by many other authors, including R. Schmidt (12), O. Gerngross and H. Herfeld (13), L. Pollak and A Patzenhauer (14), L. de Hessell (15), A. Küntzel (16), R. Lauffman (17), and F. Müller (18, 19). The latter's investigations were of special assistance in finding its most suitable application. The method applied by our investigators was based mainly upon the German semi-official method (20) and upon a description in Bergmann's "Handbuch" (21). The filtered analytical solution was boiled with strong hydrochloric acid, clarified by filtration, precipitated with tannin and cinchonine at 70°C. without agitation, boiled for two minutes, and the precipitate was filtered immediately, washed, dried, and weighed.

All results obtained in the first tests were very far from the true composition. It may be that these large discrepancies were caused mainly by the fact that natural tanning materials like quebracho were used instead of tannic acid. Afterwards, Dahl tried different preparations and found the best formation of precipitate in the presence of tannic acid made by General Chemical Company. Barnwell used Baker's tannic acid powder with equally satisfactory results.

Dahl applied the method to all samples of Series 1 and Barnwell to all samples of both Series 1 and 2. The results obtained are shown in Table III. All figures were calculated in the same way as in Table II.

A considerable discrepancy can be noticed between the figures of the two authors for Sample 1, Series 1. By using their figures for calculation of factors for converting the weight of precipitate into lignosulfonate percentages, the factor 1.655 can be obtained from Dahl's figures, and 1.323 from Barnwell's figures. Similar discrepancies can be found in the literature, where various figures are mentioned as converting factors, the most popular one being 1.35 (20). However, the findings of the two authors are still comparable, because they are proportionate for each sample, and deviation and relative deviation figures are fairly close. As regards the absolute size of the latter

TABLE III

LIGNOSULFONATE DETERMINATIONS WITH CINCHONINE

Author and Series	Sample No.	Grams Precipitate per 100 Grams Liquid Extract		Deviation	Relative Deviation
		Theoretical	Actual		
Dahl	1	——	31.42	——	——
No. 1	2	1.55	1.08	−0.47	−30.3
	3	22.26	24.54	+2.28	+10.2
	4	0.00	0.05	+0.05	
	5	5.30	5.69	+0.39	+7.4
			Av.	0.80	10.9
Barnwell	1	——	39.30	——	——
No. 1	2	1.93	1.27	−0.66	−34.2
	3	27.84	29.95	+2.11	+7.6
	4	0.00	0.00	0.00	0.0
	5	6.66	6.98	+0.32	+4.8
			Av.	0.77	8.5
Barnwell	L	——	25.80	——	——
No. 2	V	0.00	0.00	——	——
	1	0.82	0.48	−0.34	−41.5
	2	3.80	3.34	−0.46	−12.1
	3	0.00	0.00	0.00	0.0
	4	9.83	11.43	+1.60	+16.3
	5	2.17	1.45	−0.72	−33.2
			Av.	0.62	18.8

figures, they are not too discouraging, and they adequately prove that the findings are in reasonably close relationship with the true composition.

Both authors repeated their determinations and obtained good agreement between duplicates, whereas bad discrepancies could be noticed as long as the wrong tannin was used. This means also that the method can be made serviceable by proper control of all factors which may have an influence upon its results. These factors are the following: concentration of lignosulfonates, concentration of cinchonine, acidity of the solution, character of tannin added, temperature of precipitation, heating rate, boiling time, and agitation. Sufficient evidence could be found in the literature that the amount of hydrochloric acid should be 5 ml. per 100 ml. of solution, that the solution should be boiled two minutes after precipitation and then filtered immediately, without standing, and that all kinds of agitation should be avoided. The tests mentioned above showed what kind of tannin should be used, and thus three factors were left which were investigated by Dahl on samples of Series 2.

He investigated the influence of lignosulfonate concentration by diluting different amounts of all samples to 1000 ml., keeping all other factors unchang-

ed. His precipitation temperature was always 70°C., his heating rate 15°C. per minute, his boiling time 2 minutes, and he always used 25 ml. of 1.5% cinchonine solution and 10 ml. of 1.5% tannin solution.

In a second series he kept the lignosulfonate concentration at the same level by using the same dilutions of samples for all tests, and he varied the amount of 1.5% cinchonine solution added.

In a third series he kept both lignosulfonate and cinchonine concentrations constant, and he varied the heating rate. The speed of heating is of importance during that time only which elapses between precipitation at 70° and start of boiling, but it is more easily measured during the first period when the solution is heated up to 70°C. without cinchonine. Dahl observed the rise of temperature on a thermometer immersed in the solution at a certain position of the electric heater switch (which can be substituted by a certain length of gas flame) during the time when the temperature was being raised to 70°C., and he applied heat at the same rate until boiling was finished.

In order to determine the influence of concentration upon the results, it has to be considered first how much solid lignosulfonate and how much solid vegetable extract each sample of Series II contained. These data are contained in Table IV, and also the theoretical yield of precipitate which should be obtained from 100 grams of the liquid sample by applying the factor 1.35.

TABLE IV

COMPOSITION OF SAMPLES OF SERIES II

Sample No.	Total Solids %	Lignosulfonates %	Vegetable Extract %	Theoretical Yield of Precipitate Obtainable from 100 Grams Liquid Blend Grams
L	31.40	31.40	0.00	23.26
V	34.10	0.00	34.10	0.00
1	34.01	1.01	33.00	0.75
2	33.66	4.97	28.69	3.69
3	34.10	0.00	34.10	0.00
4	33.06	11.97	21.09	8.87
5	34.10	2.88	31.22	2.13

Based upon the above data, Dahl's results are evaluated in Table V. The first column indicates the quantity of sample diluted to 1000 ml., the second and third ones the grams lignosulfonate and vegetable extract present in the analysis. The quantity given in the first column was always diluted to 1000 ml., and 50 ml. of this dilution were taken for the analysis; therefore, the figures of the second column were calculated by multiplying the numbers in the first column by the corresponding lignosulfonate percentages of Table IV and dividing by 20; for those of the third column the vegetable extract percentages of Table IV were used. The fourth column contains the weights

of precipitates, related to 100 grams of the original liquid blend. The fifth column contains the deviations against the corresponding theoretical yields of Table IV. The sixth column contains relative deviations, calculated the same way as in the case of methoxyl.

TABLE V

INFLUENCE OF CONCENTRATION UPON THE RESULTS OF THE CINCHONINE METHOD

Grams Substance in 1000 ml.	Sample No.	Grams Lignosulfonate Present in the Analysis	Grams Extract Present in the Analysis	Grams Precipitate per 100 Grams Substance	Deviation %	Relative Deviation %
50	L	0.7850	0.0000	16.54	−6.72	−28.9
	V	0.0000	0.8525	0.00	0.00	0.0
	1	0.0252	0.8250	0.78	+0.03	+4.0
	2	0.1242	0.7172	3.81	+0.12	+3.3
	3	0.0000	0.8525	0.00	0.00	0.0
	4	0.2992	0.5272	9.49	+0.62	+7.0
	5	0.0720	0.7805	1.62	−0.51	−23.9
25	L	0.3925	0.0000	22.35	−0.91	−3.9
	V	0.0000	0.4262	0.00	0.00	0.0
	1	0.0126	0.4125	0.57	−0.18	−24.0
	2	0.0621	0.3586	3.82	+0.13	+3.5
	3	0.0000	0.4262	0.00	0.00	0.0
	4	0.1496	0.2636	9.56	+0.69	+7.8
	5	0.0360	0.3902	1.46	−0.67	−31.5
15	L	0.2355	0.0000	22.85	−0.41	−1.8
10	L	0.1570	0.0000	24.52	+1.26	+5.4
	V	0.0000	0.1705	0.00	0.00	0.0
	1	0.0050	0.1650	0.55	−0.20	−26.7
	2	0.0248	0.1434	3.21	−0.48	−13.0
	3	0.0000	0.1705	0.00	0.00	0.0
	4	0.0598	0.1054	9.19	+0.32	+3.6
	5	0.0144	0.1561	1.45	−0.68	−31.9
7.5	L	0.1177	0.0000	24.41	+1.15	+4.9

These figures lead to the same conclusion as those of Table III, namely that the method can be considered serviceable under any conditions, even if the concentration has not been chosen properly. Deviations are within the limits of $\pm 30\%$ of the true value, and this is fairly good accordance, considering that technical spruce consists of many different substances of different character and chemical behavior and that some discrepancies of similar magnitude could be found even among the corrected figures of methoxyl determination.

However, the table also proves that the discrepancies of the method are increased badly by going beyond certain limits of lignosulfonate concentration, whereas the vegetable extract content does not have too much bearing upon the results. Among the values contained in Table V, 17 determinations were carried out on samples containing lignosulfonates. (Those samples whose lignosulfonate content was zero are of no importance for this investigation.) These 17 determinations can be grouped as follows:

In one case (50: L) the quantity of lignosulfonate present in the analysis was above 0.4 gram. Relative deviation was 28.9%.

In seven cases (50: 2,4; 25: L, 4; 15: L, 10: 1, 7.5: L) the lignosulfonate was between the limits 0.1 to 0.4 gram. In this range the maximum of relative deviation was 7.8%, and the average, calculated by dividing the numerical sum of deviations by the sum of theoretical precipitate yields (from Table IV), was 4.5%.

In nine cases (50:1,5; 25: 1,2,5; 10: 1,2,4,5) the lignosulfonate was below 0.1 gram. In this range the maximum of relative deviation was 31.5% and the average 12.9%.

This makes it quite evident that 0.1–0.4 grams solid lignosulfonate should be present in the analysis in order to obtain most reliable results. Therefore, the amount of solid or liquid blend to be diluted to 1000 ml. should be so chosen, by a preliminary determination, that it contains 2–8 grams solid lignosulfonate.

Dahl tested the influence of cinchonine concentration in a similar manner, by adding 10, 25, and 50 ml. of 1.5% cinchonine solution respectively to the same amount of all samples. 10 ml. was definitely not sufficient to complete the precipitation, and all weights obtained were too low. 50 and 25 ml. yielded similar results, the average of the 25 ml. figures being somewhat closer to the truth.

By examining the influence of heating rate he found that quick heating, i. e., raising the temperature by 25°C. per minute, yields low values, and that the heating rate of 15°C. per minute is most favorable.

Dahl also stated that the proper drying time for the precipitate obtained is three hours. The weight obtained in this time does not change appreciably by drying overnight.

It is well known from the literature that the cinchonine method has many weaknesses. Cinchonine and lignosulfonates do not react in stoichiometric proportions and the precipitate may contain various percentages of both of them, as shown by Küntzel's investigations (16). Deviations may be caused by different molecular sizes, different degree of sulfonation, and by more or less complete precipitation of lignosulfonates. In spite of these faults, the method has been used successfully for the estimation of lignosulfonate, and the above investigations prove that it is a suitable method for indicating their quantity in good approximation.

These investigations prove that no precipitate—or, in one exceptional case, only a very small amount of it—was obtained when no spruce was present in the solution. They also prove that the quantity of precipitate is in definite relationship to the quantity of lignosulfonate present. Certain discrepancies are unavoidable, but their magnitudes are within reasonable limits, and they can be lessened by choosing the proper amount of sample.

It has been mentioned before that certain problems in connection with the methoxyl determination have to be cleared up before it can be made workable. It will be shown later that Barnwell's method also needs more investigation. The application of paper chromatography is still nothing more than an uncertain hope. Therefore, in order to satisfy the actual need of a method which indicates the lignosulfonate content at least approximately, the cinchonine reaction is recommended for provisional adoption. All details of this method are sufficiently cleared up by now and there is little hope that further investigation be directed towards the three above-mentioned methods, and as soon as any one of them can be made workable, so as to yield reliable results of high accuracy, it should be introduced to replace the cinchonine reaction. In case these investigations should fail to produce a serviceable method, the cinchonine reaction should be finally adopted as official.

The following procedure is recommended:

Reagents Required: (*a*) Tannin solution: Dissolve 15 grams of tannic acid C. P. in hot distilled water and make up to 1000 ml. (*b*) Cinchonine solution: Agitate 15 grams of cinchonine in 100 ml. distilled water, and add conc. sulfuric acid drop by drop until perfect solution is obtained. Make up to 1000 ml. with distilled water.

Preparation of Substance for the Analysis: Weigh an amount of substance which contains approximately 2–8 grams solid lignosulfonates. Dissolve and dilute to 1000 ml. according to the ALCA specifications for vegetable extracts. Filter the solution through a Whatman 41H or similar rapid paper, without paying attention to the clarity of the filtrate. To 100 ml. of the filtrate add 5 ml. conc. hydrochloric acid, heat to a boil, keep boiling for two minutes, cool, and make up to 100 ml. Filter the solution through an S&S 610 or similar paper to absolute clarity, using one gram of Hyflo Supercel (Johns-Manville) or similar filter aid.

Procedure: Put 50 ml. of the filtrate into a 250-ml. beaker, add 10 ml. of the tannin solution, control the temperature with a thermometer, and regulate the source of heat so that the temperature of the liquid is raised by not more than 15°C. per minute. When 70°C. is reached, remove the thermometer, and add 25 ml. cinchonine solution from a pipet whose tip touches the side of the beaker just above the surface of the liquid. Without changing the heat control, continue heating until boiling has definitely started, and keep boiling for two minutes. All kinds of agitation must be strictly avoided

during the reaction. After two minutes boiling pour the liquid immediately through a large porosity glass filter crucible (Corning EC), bring the sticky lump of precipitate onto the filter, wash with hot water, dry for 3 hours at 100°C., and weigh.

$$\text{Lignosulfonate percentage} = \frac{2000 \times \text{Weight of precipitate} \times 1.35}{\text{Weight of sample}}$$

Barnwell's Reaction. Because of the favorable results obtained by this method as a qualitative test, it appeared very natural to try to apply it for quantitative estimation, too. This was done by S. Dahl and J. M. Hinkle.

The main difficulty they found was that the precipitate is hard to filter and cannot be separated from the solution. Both investigators used different methods to overcome this difficulty. Hinkle precipitated at the boil, and in this way he obtained the precipitate in a form which could be filtered well. His tests showed that filtration after standing and cooling down of the solution is preferable to hot filtration, but in both cases he noticed after-precipitation in the filtrate. To prevent this, he tried one hour digestion on the steam bath according to Barnwell's suggestion, but some after-precipitation still could be observed. He found that 2 hours digestion at room temperature, followed by 1 hour digestion on the steam bath gave the best results.

This method was used in the tests reported in Table VI with the following variations in the final operations:

Cold Method: After steam-bath digestion let stand until cold, filter, wash with cold water, dry, and weigh.

Hot method: After steam-bath digestion filter immediately, wash with hot water, dry, and weigh.

Gooch crucibles were used for filtration in all tests.

He also tested the influence of concentration. In all cases 50 grams of substance were dissolved, acidified with 125 ml. conc. hydrochloric acid, and made up to 1000 ml. The solution was allowed to stand for two days, and then the supernatant liquid was used. Generally 25 ml. of solution were taken and mixed with 75 ml. water and 50 ml., of Barnwell's Reagent (see "Qualitative Tests"). However, in some cases, when the lignosulfonate concentration appeared to be low, 100 ml. were taken from the supernatant liquid and mixed with Barnwell's Reagent without adding water.

It is quite apparent from these results that by hot filtration part of the precipitate is dissolved, and that all procedures should be carried out cold. The use of amounts higher than 25 ml. is absolutely not permissible. The results of the cold method are, to a certain extent, proportional to the true composition, but there are considerable discrepancies, the worst of these being the fact that precipitates were found in blends which contained no lignosulfonates. One of the factors causing these troubles has been mentioned

TABLE VI

J. M. HINKLE'S INVESTIGATIONS OF BARNWELL'S REACTION

Description of Test	Series No.	Sample No.	Grams Precipitate per 100 Grams of Total Solids	Lignosulfonate Content Calculated from the Precipitate of the Sample Consisting of Straight Lignosulfonate %	True Lignosulfonate Content (Table I) %
Cold Method	1	1	24.377		100.00
25 ml.		2	1.1793	4.84	5.81
		3	15.6488	64.19	74.33
		4	0.5478	2.25	0.00
		5	4.8365	19.84	21.63
Cold Method	2	L	26.0859		100.00
25 ml.		V	0.8716	3.34	0.00
		1	0.9714	3.52	2.98
		2	2.5672	9.84	14.75
		3	0.7677	2.94	0.00
		4	6.4019	24.54	36.20
		5	1.6686	6.40	7.82
Cold Method	2	V	2.6548	10.18	0.00
100 ml.		1	2.9989	11.50	2.98
		3	2.4520	9.40	0.00
		5	4.3642	16.73	7.82
Hot Method	1	1	22.0044		100.00
25 ml.		2	0.2200	1.00	5.81
		3	12.4942	56.78	74.33
		4	0.0000	0.00	0.00
		5	2.7852	12.66	21.63
Hot Method	2	L	24.1335		100.00
25 ml.		V	0.1950	0.81	0.00
		1	0.1262	0.52	2.98
		2	0.8326	3.45	14.75
		3	0.1264	0.52	0.00
		4	3.9541	16.38	36.20
		5	0.3797	1.57	7.82

in the first part of this paper: after longer standing, precipitates can be observed even in straight vegetable blends. Besides this, heating of the solution on the steam bath and drying of the precipitate cause decomposition, and thus the final weight does not indicate the true amount of precipitate.

In order to avoid all these troubles, S. Dahl followed this procedure: 50 grams substance were dissolved, acidified, and diluted to 100 ml. as above. 25 ml. were taken right after dilution, and clarified in a centrifuge tube at about 2500 rpm. The clear liquid was transferred to a tared centrifuge tube, 10 ml. of Barnwell's Reagent was added with stirring and, after centrifuging

a few minutes at 1200 rpm, most of the liquid was poured off. To the sediment remaining in the tube 25 ml. of water and 10 ml. of Barnwell's Reagent were added with stirring, in order to wash the sediment. After centrifuging again at 2500 rpm for a few minutes, the liquid was poured off, and the tube with the sediment was placed upside down to drain. After about one hour it was wiped dry on the outside and on the inside down to the sediment, and weighed. Wiping and weighing were repeated until successive weighings indicated negligible changes only.

Dahl noticed that the precipitate was contaminated with some vegetable extract material, as shown by the fact that some sediment was obtained from extracts containing no lignosulfonates at all. This material could be washed out in the second centrifuging, provided that the sediment had not been packed too hard. This was the reason for centrifuging at comparatively slow speed the first time.

Table VII shows results obtained.

TABLE VII

S. DAHL'S INVESTIGATIONS OF BARNWELL'S REACTION

Series No.	Sample No.	Amount of lignosulfonate actually found %	True lignosulfonate content (Table I) %
1	2	2.8	5.81
	3	81.9	74.33
	4	1.2	0.00
	5	12.0	21.63
2	V	0.0	0.00
	1	2.5	2.98
	2	14.6	14.75
	3	0.0	0.00
	4	46.6	36.20
	5	6.1	7.82

All percentages were calculated by dividing the weight of the sediment by the weight found in the same amount of pure lignosulfonate sample, as in Table VI.

Apparently the method had been elaborated and worked better when the samples of the second series were tested. This makes it probable that further improvement can be expected; for example, use of vacuum and desiccants for drying, instead of wiping, may help to obtain more reliable results. In continuing these investigations, it is important also that heating be carefully avoided, and that the precipitate be separated from the solution quickly. Under those conditions, favorable results can be obtained, which may make Barnwell's method suitable for official adoption.

SUMMARY

(*a*) The following reactions were rejected as unsuitable for detection of lignosulfonates: the color reactions of Tingle, van der Hoeven, Grasser, and the aniline precipitation of Procter and Hirst in its original form.

(*b*) Promising tests were made with Barnwell's reagent, and the necessity of further investigation is emphasized. Such investigations may make it the most suitable reagent for qualitative detection and even for quantitative estimation of lignosulfonate.

(*c*) Kilchner's chromatographic method cannot be considered serviceable in its present form, but further investigation is recommended.

(*d*) The presence of methoxyl groups cannot be considered as qualitative proof of the presence of lignosulfonates, and serious difficulties were encountered in applying the determination of methoxyl groups to the quantitative determination of lignosulfonate. Further investigations are urgently recommended, mainly because the high precision of this procedure makes it particularly attractive.

(*e*) According to the tests carried out by our members, the following reactions were considered most reliable under present circumstances:

For qualitative detection: Gerngross' modification of the Procter-Hirst reaction.

For quantitative estimation: the cinchonine reaction.

These two methods are recommended for provisional adoption.

REFERENCES

1. Tingle, A. *Analyst*, **60**, 86 (1935); abstracted in *JALCA*, **31**, 454 (1936).
2. Hoeven, C. van der. *Nederl. Leder-Ind.* (1935), **41**, Suppl. 1365-7; **46**, Suppl. 1371-2; **52**, Suppl. 1373-4; abstracted in Bergmann-Grassmann, *Handbuch der Gerbereichemie, II*, Part 2, 576, (Vienna: Julius Springer, 1939) and in *JALCA*, **32**, 342 (1937).
3. Grasser, G. *Handbuch fur Gerberei-Laboratorien*, 3rd ed., Vienna (1929); abstracted in Bergmann-Grassman, op. cit., II, Part 1, 223, and Part 2, 576.
4. Kilcher, H. *Paper Chromatography and Tannins*, ed. Geigy Chemical Works, Schweizerhalle, Switzerland.
5. Martin, H. *Bull. Assoc. Franc. Chimistes Inds. Cuir*, **13**, 58 (1951).
6. Procter, H. R. and S. Hirst. *J. Soc. Chem. Ind.* **28**, 293 (1909).
7. Zeisel, S. *Monatshefte* **6**, 989 (1885) and **7**, 406 (1886).
8. *Scott's Standard Methods of Chemical Analysis,, II*, (5th ed.) ed. N. H. Furman, p. 1892. New York: D. Van Nostrand Co. (1939).
9. Viebock, F. and A. Schwappach. *Ber.* **63**, 2818 (1930); Viebock, F. and C. Brecher. *Ber.* **63**, 3207 (1930).
10. *Scott's Standard Methods*, p. 2527.
11. Appelius, W. and R. Schmidt. *Collegium* (1914), 597 and 706.
12. Schmidt, R. *Sulfit-Cellulose-Extrakte* (1930), 6.
13. Gerngross, O. and H. Herfeld. *Collegium* (1933), 66 and 441.
14. Pollak, L. and A. Patzenhauer. *Collegium* (1939), 379.

15. Hesselle, L. de. *Collegium* (1921), 425.
16. Küntzel, A. *Collegium* (1935), 593.
17. Laufmann, R. *Collegium* (1924), 121.
18. Hesselle, L. de. *Collegium* (1929), 6.
19. ———. *Ibid.* (1932), 711.
20. VAGDA Kalender (Gerbereichemisches Taschenbuch) (3rd ed.) ed. H. Küntzel, pp. 207-09. Dresden and Leipzig:Theodore Steinkopf (1932).
21. Bergmann-Grassmann. *Op. cit.*, II, Part 2, 570.
22. Gerngross, O. *Collegium* (1932), 244. See also VAGDA KALENDER (1932), 84.
23. Noll, A. *Papier-Fabr.* **36** (Tech T1), 41-5 (1938).
24. Steven, O. L. Ger. Pat. No. 514723 and U. S. Pat. No. 1750732, abstracted in Bergmann-Grassman, *op. cit.*, II, Part 2, 560.
25. Klason, P. *Ber.*, **53**, 706 and 1862 (1920)
26. Gustavson, K. H. *Ing. Vetenskaps Akad., Handl.* (*Proceedings of the Royal Swedish Institute for Engineering Research*), **177**, 62 (1944).

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Our grandfathers and grandmothers would be amazed to see the calfskin shoes of today. When they were wearing calfskin (remember how proud "Little Women" were of their stout new calfskin boots?), this shoe material was tanned with hemlock bark, stuffed with tallow and waxed on the flesh side. There were no modern aniline dyes, colored leathers were limited, and the beautiful, distinguishing calf grain of modern leather was hidden from view.—Ruth H. Kerr. *Calf Leather from the Gay Nineties to the Frenzied Forties* (from ENCYCLOPEDIA OF THE SHOE AND LEATHER INDUSTRY, Hide and Leather Publishing Co., 1941.)

"There's nothing like leather" is a proverbial expression in English and other languages to ridicule an exaggerated opinion of the value of one's own *métier*. The allusion is to the old fable accredited to Aesop, of the town in danger of a siege, wherein, at a hasty consultation of the citizens as to the best method of fortification, the mason recommends stone, the carpenter good stout oak, and the currier, last of all, gets up and says that he has found there is nothing like leather.

The popularity of the fable, and so of the phrase, has been largely influenced by the following anonymous rhymed version, which was found in most of the school-books in the earlier portion of the century:

A town feared a siege, and held consultation
Which was the best method of fortification;
A grave, skillful mason said in his opinion
Nothing but stone could secure the dominion.
A carpenter said, "Though that was well spoke,
It was better by far to defend it with oak."
A currier, wiser than both these together,
Said, "Try what you please, there's nothing like leather."

—*Handy Book of Literary Curiosities*, William S. Walsh, J. B. Lippincott Company, Philadelphia, 1905.

Automatic End Point Detection for Water-Penetration Test E42

Report of the Water Penetration Subcommittee

MIETH MAESER

United Shoe Machinery Corporation
Beverly, Massachusetts

ROBERT M. LOLLAR

Dept. of Basic Science in Tanning Research
Tanners' Council Research Laboratory
University of Cincinnati
Cincinnati, Ohio

ABSTRACT

In order to reduce the possibility of operator error and eliminate the necessity of constant operator attention when testing highly resistant leathers with the Maeser water-penetration machine, a method for automatic end point determination was developed. This method was based on the sudden change in the electrical resistance between the inside and the outside of the leather at the instant that some point was completely wet through. Comparative tests were made on untreated leather, low-level Sylflex leather and high-level Sylflex leather using visual end point determination, automatic end point determination and automatic end point determination with a load on the inside of the trough. The water pick-up by the specimen and by the wick in the trough were measured at two levels of exposure (10,000 and 40,000 cycles.)

The results indicate the automatic end point determination under load to be the most severe method and the visual method to be least severe. The tests further indicate that too much emphasis may have been put on end point detection and too little on water absorption by the specimen and by the wick.

Leather given the medium treatment was penetrated in a rather small number of cycles and yet the leather was effectively waterproofed as indicated by water pick-up. The amount of water passed through medium-treated leather was far less than untreated leather and an effective water barrier had been made. The cycles to penetrate seem to be an unrealistic measure of the effectiveness of the treatment.

INTRODUCTION

The Water Penetration Subcommittee attempted, in 1954–55, to study the effect of the speed of testing on the results obtained with the Maeser machine. It soon became obvious that the worst drawback to the machine, when testing highly resistant leather, was the necessity of keeping the test under close operator attention so that the end point could be observed with reasonable accuracy. The Subcommittee suggested that some means should be found for the automatic determination of the end point before other evaluation of the test was attempted.

The writer, with the cooperation of members of the Electronic Department at the United Shoe Machinery Corporation, made a number of preliminary tests involving changes in various electric and dielectric constants of the leather as it was being tested to determine the property most suitable for this purpose. These tests indicated that the resistance between the inside and the outside of the leather trough remained high until the instant that some point wet completely through and then dropped abruptly. This property was, therefore, satisfactory for this purpose.

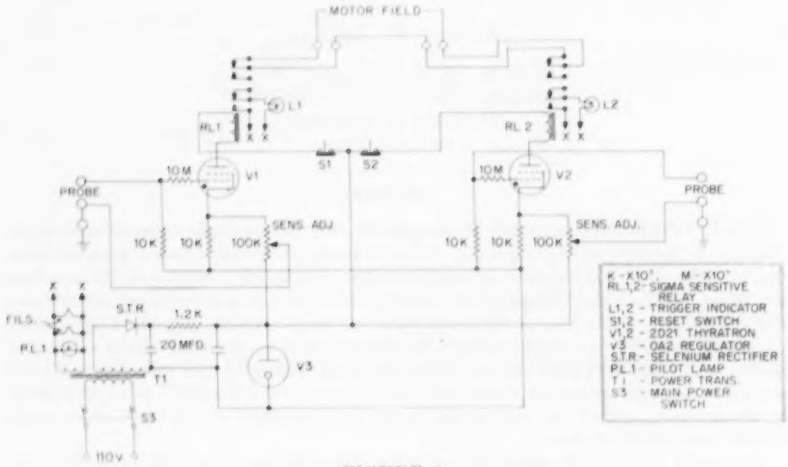


FIGURE 1.

A short test program was set up to evaluate several ways of using the change in resistance as a means of determining the end point. The methods described below appeared more closely to simulate the conditions inside a shoe and to give a surer indication of penetration than other methods which used metal foil, balls, chain, or other such materials in the trough.

Dr. Lollar was asked to plan tests which would give a satisfactory comparison between visual determination of the end point and two modifications of a method using the change in resistance.

EXPERIMENTAL END POINT DETECTION

Method A.—This is the common visual method in which the end point was determined by observing the number of machine cycles at which the first bead of water or the first wet spot appeared inside the trough.

Method B.—The water tank was filled with a 1% solution of NaCL. A wick of machinists' waste was degreased in Acetone, dried, saturated in a 1%

NaCL solution, wrung as dry as possible by hand, then placed in the trough formed by the specimen in the machine. An electronic device with a circuit as shown in Figure 1 was constructed and cut into the power line to the motor. One leg of the probe was clipped to the damp wick inside the trough. The other leg was hung in the water tank.

It was previously determined that when a small bundle of the damp wick fibers were allowed to contact the salt solution in the water tank, the circuit had a resistance of approximately 4000 ohms. The electronic device was set so that if the resistance through the leather between the wick and the bath became less than 5000 ohms, the power line was cut and the motor stopped.

The wick was covered with cellophane to reduce evaporation during the test.

The electronic device is so built that if the resistance across either testing head drops below 5000 ohms, the machine stops and a light indicates the specimen that has wet through. When the wire is removed from either the water tank or the wick of the penetrated specimen, the machine can again be started, and the run on the other specimen can be continued until it also fails.

Method C.—This method is like Method B in all respects except that two lengths of ½″ roller chain, 3½″ long, were laid on top of the wick as a load to force it into closer contact with the specimen.

In this test, the cellophane did not cover the specimen quite as well as in test "B".

Machine.—The machine used was the Murmac model of the Maeser machine. The testing rate was 200 rpm. End plates were used on the head *V*'s to keep water from contacting the end of the specimen. The clamp wedges were made of 70 to 75 durometer neoprene rubber.

The brass fork with a rubber insert used regularly in the machine was not used as it was necessary to remove all metal from inside the trough in order to completely insulate the wick from any machine part which had contact with either the water or the water tank.

The machine had a 1″ testing stroke.

Leather.—The leather used in the tests was 5–5½ oz. chrome-tanned side leather, tanned, finished and treated by A. C. Lawrence Co.

Water Resistance Levels.—Three levels of water resistance were used:

(*a*) Untreated
(*b*) Low-level Sylflex
(*c*) High-level Sylflex

Specimens.—For each level of water resistance, the following specimens were used:

A piece of leather 15″ square was cut from the central part of each of three sides. One edge of the piece was cut parallel to and 3″ away from the backbone. Each piece was then laid out in 9 blocks 4″ x 4 ¾″ with the long dimension parallel to the backbone.

The blocks were lettered A, B or C as noted in Figure 2.

	Backbone Direction ⟵⟶		
Hide 1	A_{11}	B_{11}	C_{11}
	B_{12}	C_{12}	A_{12}
	C_{13}	A_{13}	B_{13}
Hide 2	C_{21}	A_{21}	B_{21}
	A_{22}	B_{22}	C
	B	C	A
Hide 3	B_{31}	C_{31}	A_{31}
	C	A	B
	A	B	C

FIGURE 2.—Location of specimens

The pieces marked A were tested by Method A; those marked B, by Method B; and those marked C, by Method C.

Method of Test.—End point determination was made by Method A, B, or C, as described above, except that no specimen was run more than 40,000 cycles, even though it did not wet through.

Water picked up by specimens was determined by weighing the conditioned specimen before test and after 10,000 cycles, the difference in the two weights being the weight of the water absorbed by the specimen.

Weight of water picked up by the wick is a measure of the amount of free water actually pumped through the leather. The wick was saturated, wrung out by hand, and weighed. It was then placed in the trough of the specimen and covered with a cellophane sheet. After the machine had run either 10,000 or 40,000 cycles, the wick was again weighed. The difference in the two weights was the amount of free water which passed from the water tank to the inside of the trough. If the amount of water which passed through the specimen was less than the amount which was absorbed by the specimen and the amount which evaporated from the wick, this value was negative.

Effect of Repeated Tests.—After the tests were completed, the specimens were stored for approximately 3 weeks in the standard atmosphere and the tests repeated on the same specimens. This was done twice to study the effect of repeated wetting and drying on the water resistance.

Effect of Detergents.—After the specimens were tested the third time, they were reconditioned and retested in the same way except that Seaboard Chemical Deeter was added to the salt solution in the ratio of 1 ml. of Deeter per liter of solution.

RESULTS

The results of the first run are given in Tables I–V.

By the method of tabulation used, the method of end-point determination, the end point or other value, and the location from which the specimen was cut are shown for each specimen. Thus $\frac{A}{398}$ in the first space of Table I indicates that the end point was determined by method A to be 398 machine strokes.

Repeated tests had so little effect on either the end point, water absorbed by the specimen, or the water absorbed by the wick, that it was considered useless to tabulate these results.

The use of a detergent in the water nearly destroyed the effect of the treatment. Even the most resistant leathers wet through in less than 1000 cycles. The amount of water absorbed by the specimen and by the wick was not determined.

Dr. Lollar agreed to analyze and evaluate the results. His comments are as follows: "First, the three methods read differently at the different levels of resistance. The results for cycles for initial penetration for all three methods on the untreated leather are such that the three methods can*not* be said to be different. However, on the most resistant leather, Method A is the least severe on the leather. There is a fair probability that this is true for the intermediate level of resistance. Over-all, therefore, I would rate the methods A, B, C with A being the least severe on the leather and tending to give higher cycles for penetration than methods B or C. The end point detection method has a real influence on the water uptake values by the specimens at all three water-resistance levels. Method A is the least severe on the leather treated for medium and full resistance. However, method C is the least severe on untreated leather. Over-all, I would, however, rate the methods A, B, C, with A causing less water uptake by the leather. Results at 40,000 flexes confirm this for the treated leathers.

"The data on water passed through the leather are not analyzable rigorously. End point detection methods may rank A, B, C, with A passing more water, but this must not be considered to be rigorous since there are so many negative values.

TABLE I

END POINT—CYCLES TO WET THROUGH OR SHUT OFF MACHINE

	No Treatment			Medium Treatment			Full Treatment		
Hide 1	A	B	C	A	B	C	A over	B	C
	398	252	310	22,300	16,085	6,190	40,000	20,190	27,480
	B	C	A	B	C	A	B	C	A
	546	368	490	20,180	7,320	22,190	25,570	11,740	over 40,000
	C	A	B	C	A over	B	C	A over	B
	393	304	396	11,440	40,000	15,031	16,410	40,000	26,140
Hide 2	C	A	B	C	A	B	C	A over	C
	623	342	397	9,410	15,600	11,300	8,800	40,000	35,990
	A	B	C	A	B	C	A over	B	C
	489	559	669	15,803	9,100	10,850	40,000	20,630	13,800
	B	C	A	B	C	A	B	C	A over
	368	279	486	11,630	10,380	9,486	24,390	11,840	40,000
Hide 3	B	C	A	B	C	A	B	C	A over
	422	456	590	3,890	6,210	5,200	14,850	13,990	40,000
	C	A	B	C	A	B	C	A over 40,000	B
	426	610	334	11,080	6,100	4,900	15,340		16,850
	A	B	C	A	B	C	A over	B	C
	772	312	524	3,228	4,060	5,170	40,000	18,900	15,160
Av. A	498			12,500			over 40,000		
Av. B	398			10,700			22,600		
Av. C	483			8,700			14,950		

A—Visual End Point
B—Experimental End Point—No load on wick
C—Experimental End Point—Loaded wick

"In over-all summary, therefore, it seems that method A is less severe on the leather in terms of cycles to penetrate and water uptake by the leather. However, it may be that it permits more water to flow through the leather once penetration has occurred than do the other two methods.

"All in all I prefer method C because of its severity. However, I wonder what your thoughts are about the correlation of the results with actual wear

TABLE II

AMOUNT OF WATER PICKED UP BY SPECIMEN IN 10,000 MACHINE STROKES

Weight of Water in Grams—Machine equipped with end plates

	No Treatment			Medium Treatment			Full Treatment		
Hide 1	A 3.9	B 3.9	C 3.9	A 0.4	B 1.0	C 1.7	A 0.4	B 0.7	C 1.0
	B 3.5	C 3.6	A 3.5	B 0.9	C 1.5	A 0.4	B 0.9	C 1.0	A 0.5
	C 3.4	A 3.4	B 3.8	C 1.6	A 0.5	B 1.5	C 1.0	A 0.6	B 1.0
Hide 2	C 3.7	A 4.0	B 4.2	C 1.8	A 0.4	B 1.1	C 1.1	A 0.3	B 0.6
	A 3.7	B 4.8	C 3.5	A 0.7	B 0.9	C 1.5	A 0.3	B 0.7	C 1.1
	B 4.5	C 3.7	A 3.5	B 1.1	C 1.4	A 0.5	B 0.8	C 1.0	A 0.6
Hide 3	B 4.4	C 4.3	A 4.3	B 1.4	C 1.4	A 0.7	B 0.7	C 0.9	A 0.6
	C 3.8	A 4.2	B 4.8	C 1.2	A 1.2	B 1.2	C 1.1	A 0.5	B 0.7
	A 4.8	B 4.5	C 4.0	A 0.9	B 1.4	C 2.0	A 0.4	B 0.8	C 1.0
Av. A		3.9			0.6			0.4	
Av. B		4.3			1.2			0.7	
Av. C		3.8			1.6			0.9	

A—Visual End Point
B—Experimental End Point—No load on wick
C—Experimental End Point—Loaded wick

I have always felt that the fold in the normal test is not quite severe enough to place as much pressure on the leather as occurs with wear. Hence, I have always thought that some added resistance to flexing should be used, and the wick-roller-chain cup load would give this.

"I feel that it is imperative that we secure data on initial penetration, rate of penetration and water uptake. Initial penetration values alone are

TABLE III

AMOUNT OF WATER PICKED UP BY SPECIMEN IN 40,000 MACHINE STROKES

Weight of Water in Grams—Machine equipped with end plates

	No Treatment			Medium Treatment			Full Treatment		
Hide 1	A	B	C	A	B	C	A	B	C
	Not run	Not run	Not run	1.7	1.6	2.6	0.7	1.3	1.6
	B	C	A	B	C	A	B	C	A
	Not run	Not run	Not run	2.3	3.3	1.9	1.4	2.0	1.0
	C	A	B	C	A	B	C	A	B
	Not run	Not run	Not run	2.6	0.8	3.3	1.8	0.8	1.5
Hide 2	C	A	B	C	A	B	C	A	B
	Not run	Not run	Not run	3.1	3.4	3.6	1.9	0.6	1.2
	A	B	C	A	B	C	A	B	C
	Not run	Not run	Not run	3.4	2.9	2.4	0.5	1.3	1.7
	B	C	A	B	C	A	B	C	A
	Not run	Not run	Not run	3.7	2.9	2.4	1.5	1.8	1.5
Hide 3	B	C	A	B	C	A	B	C	A
	Not run	Not run	Not run	4.0	3.6	3.0	1.5	1.5	1.0
	C	A	B	C	A	B	C	A	B
	Not run	Not run	Not run	3.1	4.0	3.8	1.9	0.8	1.4
	A	B	C	A	B	C	A	B	C
	Not run	Not run	Not run	3.6	3.6	4.0	0.8	1.4	1.5
Av. A					2.7			0.9	
Av. B					3.2			1.4	
Av. C					3.1			1.6	

A—Visual End Point
B—Experimental End Point—No load on wick
C—Experimental End Point—Loaded wick

inadequate. In fact, I believe they are the least important of the three values.

"I am not surprised at your results with a small amount of detergent in the test water bath. It is my impression that the water-resistance value of a treated leather is very sensitive to the presence of surfactants. What this means for treated leathers subsequently to be dressed back by the shoe manu-

TABLE IV

WATER PICKED UP BY WICK IN 10,000 MACHINE CYCLES

Minus Value Indicates Loss in Weight
Weight of Water in Grams—Machine equipped with end plates

	No Treatment			Medium Treatment			Full Treatment		
Hide 1	A	B	C	A	B	C	A	B	C
	10.9	10.8	4.5	Not run	−1.1	−1.7	Not run	−0.6	−1.0
	B	C	A	B	C	A	B	C	A
	13.3	5.3	11.6	−0.9	−1.4	0	−1.0	−1.0	Not run
	C	A	B	C	A	B	C	A	B
	4.7	10.3	5.8	−1.5	Not run	−1.0	−0.9	Not run	−0.9
Hide 2	C	A	B	C	A	B	C	A	B
	2.9	4.9	1.6	−0.9	Not run	+1.1	−1.1	Not run	−0.6
	A	B	C	A	B	C	A	B	C
	4.0	2.8	4.9	Not run	−0.9	−2.3	Not run	−0.6	−0.9
	B	C	A	B	C	A	B	C	A
	2.8	4.4	4.5	−0.8	−1.5	Not run	−0.6	−1.2	Not run
Hide 3	B	C	A	B	C	A	B	C	A
	6.2	7.5	12.0	−0.4	−1.2	Not run	−0.4	−0.9	Not run
	C	A	B	C	A	B	C	A	B
	2.2	8.5	8.3	−1.3	Not run	−0.7	−1.0	Not run	−0.5
	A	B	C	A	B	C	A	B	C
	10.5	5.3	3.4	Not run	−0.4	−1.0	Not run	−0.8	−1.1
Av. A		8.6			Not run			Not run	
Av. B		6.3			−0.6			−0.7	
Av. C		4.4			−1.5			−1.0	

A—Visual End Point
B—Experimental End Point—No load on wick
C—Experimental End Point—Loaded wick

facturer or the wearer by aqueous polishes, I don't know. But, really, we have no data on the true wearing value of the so-called water-resistant leathers.

"In summary, I would like to see method C or some variation thereof made a part of the water-resistance method. Then, with a more severe automatic end point detection, we can secure enough data to make a valid esti-

TABLE V

WATER PICKED UP BY WICK IN 40,000 MACHINE CYCLES

Minus Value Indicates Loss in Weight
Weight of Water in Grams—Machine Equipped with End Plates

	No Treatment	Medium Treatment			Full Treatment		
		A	B	C	A	B	C
		−0.3	−0.9	−3.2	Not run	−1.7	−2.2
Hide 1	No Untreated Specimens were carried beyond 10,000 cycles	B	C	A	B	C	A
		−0.1	−0.6	−1.0	−1.9	−2.4	Not run
		C	A	B	C	A	B
		−1.8	−0.9	0.0	−2.2	Not run	−1.6
		C	A	B	C	A	B
		−2.2	+7.5	+2.2	−2.8	Not run	−1.8
Hide 2	No Untreated Specimens were carried beyond 10,000 cycles	A	B	C	A	B	C
		+7.7	+0.2	+1.6	Not run	−1.7	−2.6
		B	C	A	B	C	A
		−0.1	+2.5	+0.1	−1.5	−2.6	Not run
		B	C	A	B	C	A
		+10.8	+1.6	+3.3	−1.2	−2.4	Not run
Hide 3	No Untreated Specimens were carried beyond 10,000 cycles	C	A	B	C	A	B
		+2.4	+1.1	+5.9	−2.6	Not run	−1.4
		A	B	C	A	B	C
		+8.0	+6.8	+6.6	Not run	−1.7	−2.2
Av. A			2.8			Not run	
Av. B			2.7			−0.6	
Av. C			0.7			−2.4	

A—Visual End Point
B—Experimental End Point—Wick not loaded
C—Experimental End Point—Loaded wick

mation of the true value of the resistance of a treated leather. The present method suffers since it is slow and requires operator attention to the end point. Hence, no one runs enough tests to secure a valid estimate of the leather character. Certainly the question of speeding up the machine could be evaluated more readily with method C than with method A.

COMMENTS

Table I indicates that the addition of the wick decreases the number of strokes necessary to cause penetration, and loading the wick causes a further decrease. This may result from two causes: (*a*) the wick could increase the severity of the fold and thus work the leather harder, and (*b*) the leather absorbs some water from the wick and thus wets some of the inside fiber leaving less leather to be penetrated from the outside. Both of these effects would be increased by loading the wick and thus establishing a more intimate contact between the damp wick and the specimen. These conditions are both met in wearing shoes where the damp sock is forced against the inside of the shoe in walking.

The negative values of Tables IV and V indicate that less water passes through the specimen from the water tank to the wick than is lost from the wick by absorption of the specimen and drying.

The test results indicate that too much emphasis may have been put on end point detection and too little on water absorbed by the specimen and by the wick.

Leathers given the medium treatment penetrated in a rather small number of cycles and yet the leather was effectively waterproofed. The leather picked up very little water, even after 10,000 machine strokes, so it remained effectively dry and would still be a good insulator against either heat or cold. The amount of water which passed through medium-treated leather was far less than the amount which passed through untreated leather. The leather has been made an effective barrier against water, and the cycles to penetrate seems to be an unrealistic measure of the effectiveness of the treatment.

ACKNOWLEDGMENTS

The writer appreciates the cooperation of Roger Tardiff of the Electronics Department of the United Shoe Machinery Corporation and Robert Perron, now with A. D. Little Company, in designing, making and evaluating the electronics-controlled device used in these tests.

Most women's shoes were made on straight lasts until about 1885.

He that makes the shoe, can't tan the leather.—Proverb.

LIFE LINES

Brief Biographies of Our Contributors

Dr. Hellmut Gnamm, well known as author of several works on tanning, has been connected for the past 33 years with C. F. Roser Co., Stuttgart-Feuerbach, manufacturers of outstanding vegetable-tanned leathers for the novelty trade.

Dr. Robert M. Lollar's biography was given in the May issue of JALCA.

Mieth Maeser, a graduate of Brigham Young University and M. I. T., has been associated with the United Shoe Machinery Corporation for over 20 years. He joined ALCA in 1941 and has served on the Physical Testing Committee and the Council.

Dr. Fred O'Flaherty, as all readers of this journal are fully aware, has been Director of the Tanners' Council Research Laboratory, University of Cincinnati, since 1930, and has contributed scores of papers to this and other journals. He has served as President of the Association, received the Alsop Award in 1945, and was awarded the Moffat Medal in 1946.

Mrs. Jean Jacobs Tancous did her undergraduate work at the University of Cincinnati, and received her M. S. from the same institution in 1949. She has been a Research Associate in the Tanners' Council Laboratory since 1949, working chiefly on the microscopy and microbiology of skin and hide. She has been a frequent contributor to JALCA.

Raw leather will stretch.—Proverb.

At Gottingen there was a shoemakers' guild as early as 1251.

The brotherhood of Paris shoemakers was established in 1370.

The tanning of goatskin leathers did not begin in America until about 1800.

The supply of domestic hides is comparatively limited. Swiss hides are of excellent quality, but we get few or none of them in this country.

—J. de Fontenelle and F. Malepeyre, *The Arts of Tanning, Currying and Leather-Dressing* (edited from the French by Campbell Morfit), Philadelphia, 1852.

ALCA NEWS

Proceedings, Reports, Notices and News
of the
AMERICAN LEATHER CHEMISTS ASSOCIATION

OFFICERS

President—E. S. Flinn, the Mead Corporation, Chillicothe, Ohio

President-Elect—E. B. Thorstensen, S. B. Foot Tanning Company, Red Wing, Minnesota

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati 21, Ohio

Council

Mieth Maeser, United Shoe Machinery Corporation, Research Division, Balch Street, Beverly, Massachusetts

Dominic Meo, Jr., Salem Oil and Grease Company, Salem, Massachusetts

E. D. Compton, Eagle-Ottawa Leather Co., Grand Haven, Mich.

Robert Stubbings, Div. of Leather Technology, Lehigh University, Bethlehem, Pa.

Robert G. Weldon, Seton Leather Co.
Newark 4, N. J.

PAST PRESIDENTS OF THE A. L. C. A.

G. A. Kerr, W. H. Teas, H. C. Reed, J. H. Yocum, F. H. Small, H. T. Wilson, J. H. Russell, F. P. Vetch, W. K. Alsop, L. E. Levi, C. R. Oberfell, R. W. Griffith, C. C. Smoot, III, J. S. Rogers, Lloyd Balderston, J. A. Wilson, R. W. Frey, G. D. McLaughlin, Fred O'Flaherty, A. C. Orthmann, H. B. Merrill, V. J. Mlejnek, J. H. Highberger, Dean Williams, T. F. Oberlander, A. H. Winheim, R. M. Koppenhoefer, H. G. Turley

Perkin Centennial Delegate

Official delegate of ALCA at the Perkin Centennial celebration in New York City next September will be Dr. Ell Dee Compton of the Eagle-Ottawa Leather Company and a member of the editorial board of JALCA. The Perkin Centennial will commemorate the discovery of the first synthetic dye—mauve—by Sir William Perkin, at the age of 18, in a makeshift laboratory in his London home, while experimenting with methods to synthesize quinine.

AUDIT REPORT of ALCA

December 31, 1955

ARTHUR W. HOLMES
Certified Public Accountant

EXHIBIT I

BALANCE SHEET AT DECEMBER 31, 1955
AND COMPARISON WITH DECEMBER 31, 1954

	December 31, 1955	December 31, 1954	Increase or Decrease * '55 over '54
ASSETS			
Current Assets:			
Cash on Hand	$ 30.34	$ 2.28	$ 28.06
Cash in Bank	13,830.46	17,464.89	3,634.43*
Accrued Interest on U.S.T. Bond	100.00	62.50	37.50
Accounts Receivable, Misc.	–0–	385.00	385.00*
Accounts Receivable, Directory	560.00	29.00	531.00
Accounts Receivable, Advertisers	1,971.10	1,827.65	143.45
Accounts Receivable, Reprints	314.00	228.75	85.25
Total Current Assets	$16,805.90	$20,000.07	$3,194.17*
Investments:			
U.S. Savings Bonds, Series F, at cost of $3700 plus accrued interest of $540 to December 31, 1955	$ 4,240.00	$ 8,110.00	$3,870.00*
U.S.T. Bonds, 2½%, Series of 1967–1972 at cost	28,495.00	28,495.00	–0–
U.S.T. Bonds, Series G. 2½% due July, 1958 at cost	5,000.00	5,000.00	–0–
U.S.T. Bonds, 2½%, series of 1963-1968 at cost	8,842.50	–0–	8,842 50
Total Investments	$46,577.50	$41,605.00	$4,972.50
Total Assets	$63,383.40	$61,605.07	$1,778.33
LIABILITIES AND CAPITAL			
Current Liabilities:			
Accounts Payable	$ 378.50	$ 1,734.15	$1,355.65*
Income Tax Withheld	218.80	208.80	10.00
Total Current Liabilities	$ 597.30	$ 1,942.95	$1,345.65*
Deferred Credits to Income:			
Dues Received in Advance	$ 439.50	$ 284.50	$ 155.00
Subscriptions Received in Advance	3,032.29	3,001.76	30.53
Total Deferred Credits	$ 3,471.79	$ 3,286.26	$ 185.53
Total Liabilities	$ 4,069.09	$ 5,229.21	$1,160.12*
Capital:			
Earned Surplus (Exhibit III)	$59,314.31	$54,375.86	$4,938.45
Reserved for Foreign Meetings	–0–	2,000.00	2,000.00*
Total Liabilities and Capital	$63,383.40	$61,605.07	$1,778.33

EXHIBIT II

STATEMENT OF INCOME

For the Years Ended December 31, 1955 and December 31, 1954

	December 31, 1955	December 31, 1954	Increase or Decrease * '55 over '54
Revenues, General:			
Dues, Journal Subs. included	$11,176.91	$10,753.50	$ 423.41
By-Laws and Methods Booklet	290.10	289.04	1.06
Directory	807.00	836.44	29.44*
Interest Income	1,167.91	1,108.52	59.39
Total General Revenues	$13,441.92	$12,987.50	$ 454.42
Revenues, Journal:			
Advertising	$12,057.45	$12,059.58	$ 2.13*
Subscriptions	5,208.81	4,892.51	316.30
Journal Sales	632.38	615.62	16.76
Reprints	1,745.94	1,900.57	154.63*
Dues, I.S.L.T.C.	957.50	995.00	37.50*
Total Journal Revenues	$20,602.68	$20,463.28	$ 138.80
Total Revenues	$34,044.00	$33,450.78	$ 593.22
Expenses, General:			
Secretary Expense	$ 4,200.00	$ 4,200.00	$ —0—
Office Operating Expense	835.38	879.91	44.53*
Uncollectable Accounts Exp.	293.50	229.90	63.60
Directory Expense	888.23	829.40	58.83
Annual Meeting Expense	449.14	186.12	263.02
Council Meeting Expenses	54.50	69.15	14.65*
Winheim Award	100.00	–0–	100.00
Auditing	175.00	150.00	25.00
Leather Chemists Union Dues	119.46	120.09	.63*
By-Laws and Methods	1,535.99	2,859.17	1,323.18*
Total General Expenses	$ 8,651.20	$ 9,523.74	$ 872.54*
Expenses, Journal:			
Printing	$15,447.57	$14,959.64	$ 487.93
Editor's Compensation	1,500.00	1,000.00	500.00
Editor's Expense	463.94	591.44	127.50*
Insurance	62.00	62.00	–0–
Storage	350.00	300.00	50.00
Miscellaneous	35.05	116.50	81.45*
Copyright Registration	48.00	48.00	–0–
Reprints	2,088.20	2,222.61	134.41*
Exchange Charges	.99	3.69	2.70*
Translations and Abstracts	249.95	350.20	100.25*
Committee Expense	81.00	36.44	44.56
Advertising Discounts Allowed	127.65	136.28	8.63*
Total Journal Expense	$20,454.35	$19,826.80	$ 627.55
Total Expense	$29,105.55	$29,350.54	$ 244.99*
Net Income	$ 4,938.45	$ 4,100.24	$ 838.21
Distributed: General	$ 4,790.72	$ 3,463.76	$1,326.96
Journal	147.73	636.48	488.75*
Total	$ 4,938.45	$ 4,100.24	$ 838.21

EXHIBIT III

STATEMENT OF SURPLUS

For the Years Ended December 31, 1955 and December 31, 1954

	December 31, 1955	December 31, 1954	Increase or Decrease *
Balance, January 1	$54,375.86	$51,275.62	$3,100.24
Add: Net Income			
General	4,790.72	3,463.76	1,326.96
Journal	147.73	636.48	488.75*
	$59,314.31	$55,375.86	$3,938.45
Deduct: Allocation to Reserve for Foreign Meetings	-0-	1,000.00	1,000.00*
Balance, December 31	$59,314.31	$54,375.86	$4,938.45

New Members

The Secretary announces the acceptance of the following new members:

ACTIVE MEMBERS

Arnold P. Barth, Chicago Rawhide Mfg. Company, 900 N. State Street, Elgin, Illinois.
Joseph A. Bassett, 31 Central Street, Topsfield, Massachusetts.
John Caporaso, Chicago Rawhide Mfg. Company, 1301 N. Elston Avenue, Chicago 22, Illinois.
Raymond Clery, Les Tanneries de Sireuil, Sireuil (Charente), France.
William E. Dooley, Brockton Cut Sole Corporation, 53 Spark Street, Brockton, Mass.
Robert G. Dow, 130 Gillette Street, Painesville, Ohio.
Don Ireno Duran, Apartado Postal No. 214, Leon, Gto., Mexico.
Aaron H. Garber, Witch City Tanning Company, Inc., 41 Mason Street, Salem, Mass.
A. Kawamura, Tokyo Noko Daigaku, P. O. D. Musashi Fuchu, Tokyo, Japan.
William J. Langley, 32 Conant Street, Danvers, Massachusetts.
William L. Law, 5043 S. Packard Avenue, Cudahy, Wisconsin.
Jekabs Linins, 94 Farewell Drive, Oshawa, Ont., Canada.
Victor Mattei, Tanners Research Laboratory, University of Cincinnati, Cincinnati 21, Ohio.
Spencer L. Parson, Jr., 3815 State Street, East St. Louis, Illinois.
Allen W. Phillips, Endicott Johnson Corporation, Endicott, New York.
Harry W. Redlich, c/o Diamond Alkali Company, Research Center, Fairport Harbor, Ohio.
Harold G. Roberts, 1749 W. Sixth Street, Red Wing, Minnesota.
Thomas E. Sinaiberger, 3324 Bishop Street, Cincinnati 20, Ohio.
Louis W. Stearns, 17 William Street, Andover, Massachusetts.
Deon Sutton, 1195 Marbro Drive, Memphis 14, Tennessee.
Michael Tenedios, 525 Bush Street, Red Wing, Minnesota.
Anthony Volante, Jr., W. Main Street, Elkland, Pennsylvania.

TRANSFERRED TO ACTIVE STATUS

Curtis L. Albee, 10 Pine Ridge Road, Reading, Massachusetts.
Richard C. Berger, 131 Broadway, Arlington, Massachusetts.
John F. Burkart, Rohm & Haas Company, 222 W. Washington Square, Philadelphia 5, Pennsylvania.
Curtis Peterson, Mansion Drive, Topsfield, Massachusetts.
Richard V. Ruffo, B. D. Eisendrath Tanning Company, P. O. Box 30, Racine, Wisconsin.

ASSOCIATE MEMBERS

Norman Berg, c/o Johannesburg Tanning Company, Pty., P. O. Sandown, Johannesburg, South Africa.
H. Franklin Brown, Robson Leather Company, Ltd., Whiting Avenue, Oshawa, Ontario, Canada.
A. Charles Chase, 266 Harrison Avenue, Manchester, New Hampshire.
Mario R. Costa, Cortume Firmino Costa S/A, P. O. Box 35, Campinas, SP, Brazil.
Rafael L. Vazques Fraga, Amarguara 316, Havana, Cuba.
George Kardos, Duclos & Payan Limited, P. O. Box 39, St. Hyacinthe, Que., Canada.
Esteban Liscano, Liscano Hnos., Carrera 1 No. 35–79, Apartado Aereo No. 12–27, Cali, Colombia.
Luis Martin Moncada G., Calle 20 Norte No. 7–33, Barrio Santa Monica, Colombia.
Leonardo Steinberg Pier, Calle del Cobre No. 135, Col. del Rastro Zona 2, Mexico, D. F., Mexico.
Dexter J. Risedorph, 57 North Blvd., Gloversville, New York.
Raymond L. Truche, Truche Leather Company, 98 Foster Street, Peabody, Massachusetts.
Carlos Villalobos, Villalobos e Hijos, Avenida de Libertad 41, Camaguey, Cuba.
G. J. Wiest, Warner Company, Cedar Hollow Laboratories, Devault, Pennsylvania.
Harold T. Woollacott, 1844 N. 73rd Street, Milwaukee 13, Wisconsin.

ALCA Elections

As a result of elections held at the annual business meeting of the Association on June 19 at Mackinac Island, Michigan, the officers and Council members of the Association are now as follows;

President—E. B. Thorstensen

President-Elect—Mieth Maeser

Secretary-Treasurer—Fred O'Flaherty

Council Members—E. D. Compton, Daniel F. Lord, Robert Stubbings, Robert G. Weldon, Frank Zeissig

ABSTRACTS

Beamhouse Problems in the Production of Fancy Leather. G. Walther. *Das Leder*, **7**, 1 (1956).—Part of a symposium on beamhouse problems. The characteristics of sheep and goat skins, and work on soaking, unhairing and degreasing such skins are reviewed. The discussion was concerned with the cause of dollar spots (some at least are the result of insect stings) and with the need for work on procollagen (soluble at pH 3–4) and tropocollagen (soluble in neutral range). I.D.C.

The Determination of Formaldehyde in Catgut. D. H. S. Forbes, J. Hunter and P. Lawrie. *Chem. and Ind.*, 129–31 (1956).—Determination of HCHO, in amounts of a few thousandths of a per cent, was accomplished colorimetrically with chromotropic acid, employing 0.1–0.2 g. samples of gut. The HCHO was either distilled from H_2SO_4 as in the Highberger-Retzsch method, into chromotropic acid, or absorbed by the chromotropic acid in a microdiffusion apparatus. In the distillation method the temperature must not exceed 150°C., otherwise HCHO is formed by decomposition of traces of carbohydrates. The microdiffusion is done at 110°C. The microdiffusion method gave results that were slightly but consistently higher than the distillation method. The standard error of the colorimetric determination was 2 micrograms. H.B.M.

Apparent Transformation of Collagen Fibrils into Elastin. D. Burton, D. A. Hall, M. K. Keech, R. Reed, H. Saxl, R. E. Tunbridge, and M. J. Wood. *Nature*, **176**, 966–9 (1955); through *Chem. Abstr.*, **50**, 5052*a* (1956).—The effects of various reagents, e.g., acids, alkalies, and enzymes, on collagen are studied. The substrates were treated with borate buffer solutions (pH 7–10.4) for varying periods of time. The electron microscope revealed a marked increase in amorphous material associated with degenerate collagen fibrils, and, by comparison with controls, an increase in structures closely resembling the fibers of elastic tissue. The longer the time of treatment, the greater the number of such structures. Similar morphological appearance was observed after treatment of collagen with 1% sodium metaperiodate in phthalate buffer of pH 5.0 at 37°C. for times ranging from 1 to 6 hr. Incubation with trypsin and chymotrypsin in phosphate buffer of pH 7.3 at 37°C. for times ranging from 3 to 24 hr. also produced elastin-like structures. Biochemical and histological studies on this material are discussed.

The Presence of d-Catechin in the Barks of the Oak and the Spanish Chestnut. W. Mayer and G. Bauni. *Das Leder*, **7**, 33 (1956).—Condensed or catechol tannins are formed from catechin under the influence of enzymes, mineral acid, dry heat, or heating in aqueous solution. These amorphous tannins are at first colorless and water-soluble but gradually develop color and become insoluble (formation of reds). Natural catechol tannins are mixtures with different degrees of condensation, so that preparation of pure materials and determination of their constitution are extremely difficult. As long as definite, individual tannins can not be isolated, only the general structure can be known, and investigators must search for simple building blocks. Fresh plant material must be used because catechins are very sensitive and rapidly react further on drying and storage. In the present work smooth (not corky) bark from freshly felled, 20-year-old trees of *Quercus sessiliflora* or *Castanea vesca* was used. For 3 days 500 grams of fresh, chopped bark were left at room temperature in 2 liters of acetone; the bark was removed by filtration, the acetone extract was concentrated to 200 ml., diluted with water to 500 ml., and extracted first with chloroform then with ether for 72 hours. Paper chromatographs showed the presence in the ether extract of d-catechin, gallic acid and two other polyphenolic substances. On evaporation of the ether, 1.8 grams of a yellow, amorphous residue remained.

Catechin showed an R_f value of 0.66± 0.02 S & S paper No. 2043b with an organic phase of ethyl acetate-glacial acetic acid-water (3:1:3) to which, after separation of the water phase, 0.5 volume parts of alcohol was added. The developing solution consisted of a mixture of 2 parts of a 10% vanillin solution in methanol and 1 part of concentrated hydrochloric acid. The ether solution was separated by partition chromatography on moist silica gel, eluting with water-saturated ether. The 270–550 ml. fraction contained pure d-catechin. When the ether solution was evaporated and the residue dissolved in hot water, 0.5 grams, equal to 0.1% of the fresh bark, of colorless, silky needles of d-catechin crystallized in a short time. After drying over phosphorus pentoxide the material melted at 173°–175°C., and the melting point was not lowered when the material was mixed with an authentic preparation of d-catechin. The pentacetyl compound melted at 131°–132°; $[a]_D^{20} = +40.7 \pm 0.8$. I.D.C.

The Action of, and a Suitable Procedure for, the Acid Pickle in the Manufacture of Fur Skins. F. Stather, H. Herfeld, and S. Beyer. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.*, **10**, 52–66 (1954).—The so-called Leipzig pickle process for furs does not in itself produce a product that is sufficiently stable towards water, but a thorough pickle is essential to impart the desired softness, pliability, and stretchiness to the pelt. Some believe that this implies the solution of considerable hide substance from the skins. In tests with rabbit skins it was found that neither increasing the amount of acid used, from 4.2 to 12.7 % H_2SO_4 on the soaked, centrifuged skin weight, nor prolonging the pickle from 20 to 60 hr., had any effect on the softness and flexibility of the pelt. Pretreatment of the skins with 2% HCHO at pH 7.8, prior to pickling, improved the properties of the pickled skins, even though nearly all the HCHO was displaced during pickling. Tests were made to determine the amounts of protein dissolved when hide powder, or rabbit skin in 2-sq. cm. squares, was treated with H_2O, 6% NaCl solution, or 6% NaCl solution containing 2–20% H_2SO_4 on the soaked weight. Roughly 5 times as much protein was dissolved from hide powder as from intact rabbit skin, but the results were otherwise similar. The NaCl solution dissolved several times as much protein as did water alone, and the salt solution containing 2% H_2SO_4 (pH 1.5) dissolved less protein than the acid-free salt solution, probably owing to precipitation of albumins by the acid. The amount of solublized protein increased with acid concentration. Pretreatment with HCHO diminished the amounts of solublized protein by 50–75%. These results, in conjunction with the improvement of properties of the pelt by pretreatment with HCHO and the lack of improvement when the acid was increased, indicate that partial solublization of collagen is not necessary to achieve the desired softness, flexibility, etc. Further pickling tests were made with NaCl, NH_4Cl, and $(NH_4)_2SO_4$ solutions, and with NaCl solutions containing formic and acetic acids, with and without HCHO pretreatment. The skins pickled with salt only were too limp to shave properly, but the properties of the finished skins that were pickled after HCHO pretreatment with salts only or with salts plus formic acid, approached the properties of normally pickled skins. Neutralization of normally pickled skins had no adverse effect except that the skins had a dryer feel. Protein solublization tests on rabbit skin squares, in solutions containing different concentrations of NaCl, with and without H_2SO_4, and with and without HCHO pretreatment, confirmed that maximum solublization was obtained at 4–5% NaCl in the absence of acid. In the presence of H_2SO_4 (pH 1.3–1.4), and for skin pretreated with HCHO, with or without acid, solublization was practically independent of NaCl concentration. Similar tests with 6% NaCl solutions containing 2–5% formic acid (pH 3.1–2.7) or 3–6% acetic acid (pH 3.8–3.5) showed that protein solublization was higher than that obtained with H_2SO_4 and decreased slightly with acid concentration for skin not pretreated with HCHO. For pretreated stock, solublization with formic acid was about the same as with H_2SO_4, and was about 10% higher with acetic acid. H.B.M.

Comparative Investigations on Different Procedures for Manufacturing Fur Skins. H. Herfeld and S. Beyer. *Ges Abhandl. Deut. Lederinsts. Freiberg/Sa.*, **11**, 60–78 (1955). See preceding abstract.—Semi-works scale tests with rabbit skins confirmed the previous finding that the Leipzig pickle alone does not yield a sufficiently water-stable product, whether the skins are afterwards neutralized or not. Tannage with HCHO or Cr gave good results under proper conditions. A combined HCHO–alum tannage had no advantage over HCHO only. Improved results were obtained by treating the skins with HCHO before pickling, even though HCHO was displaced by the pickle acid. For HCHO tannage, the HCHO is added to the pickled skins, which are later neutralized to pH 7.5–8.0. For Cr tannage the pickled skins are adjusted to pH 3, tanned with 33% basic Cr liquor containing 1.2% Cr_2O_3 on the centrifuged skin weight, and neutralized with Na_2CO_3 to 50% calculated basicity. The HCHO-tanned skins contained about 0.25% HCHO and shrank at 73°C. The Cr-tanned skins contained about 0.7% Cr_2O_3 and shrank at 77–80°C. These shrink temperatures are considered high enough for furs. The tannage is held down to the minimum consistent with reasonable stability to avoid making the pelts leathery. Neither tannage affects dyeing adversely, except that the catalytic action of Cr precludes bleaching with H_2O_2. H.B.M.

Influence of Different Mordants on the Colorability and Color Intensity of Rabbit Hair. F. Stather, S. Walther, and U. Stather. *Ges. Abhandl. Deut. Lederinsts.* Freiberg/Sa., **12**, 82–6 (1955).—Rabbit hair was dyed with Ursol dyes after mordanting with one of the following mordants: (*a*) none, (*b*) $K_2Cr_2O_7$ + acetic acid, (*c*) same plus sodium acetate, (*d*) $K_2Cr_2O_7$ adjusted to pH 7 (monochromate), and (*e*) $FeSO_4$ + acetic acid. Examination of cross sections of the dyed skins showed: (*a*) no dye takeup without mordant, (*b*) dyeing of the medulla only with iron mordant, and (*c*) dyeing of the cortex with Cr mordants. The optimum pH value for intensity of coloration and complete penetration was about 4. To get good penetration through the cortex the H_2O_2 used to develop the dye should be added to the dye bath after 45 min. rather than immediately. H.B.M.

Colorimetric Determination of Primary Aliphatic Amines by Copper Salicylaldehyde Method. F. E. Critchfield and J. B. Johnson. *Analytical Chemistry*, **28**, 436 (1956).—A new method for the determination of primary aliphatic amines in the presence of secondary and tertiary amines is described. The primary amine is made to react with an aqueous reagent containing cupric chloride, salicylaldehyde, and triethanolamine. The copper salicylaldehydeimine formed in this reaction is extracted into 1-hexanol. The amount of copper in the hexanol layer, which is determined colorimetrically by reaction with bis(2-hydroxyethyl) dithiocarbamic acid, is a measure of the primary amine in the sample. The method has been successfully applied to 15 amines. Data for the analysis of several amine mixtures are given. In most cases an accuracy within 5% can be expected. Interfering compounds and those which fail to react are discussed. Authors' abstract.

Color Reaction of Amino Acids with Alloxan, Isatin, and Ninhydrin in Circular Paper Chromatography. A. Saifer and I. Oreskes. *Analytical Chemistry*, **28**, 501 (1956).—Color reactions of 51 amino acids and their sensitivities were determined as spot tests on filter paper with alloxan, isatin, and ninhydrin. R_f values for these amino acids were obtained with the circular chromatographic method using phenol- and butanol-acetic acid as developing solvents. Alloxan gave stable and uniform colors for most amino acids and was a more sensitive reagent than ninhydrin for some of them. For amino acids with similar R_f values, simultaneous use of these reagents applied to sectors from one chromatogram often permits the "differential" determination of a single amino acid in a mixture.

Isatin is the most useful for this purpose because of the wide variety of its color reactions and lack of reactivity with many amino acids. The nature of these color reactions for amino acids and their possible application to amino acid mixtures are discussed

Authors' abstract.

Colorimetric Determination of Hydroxyproline. D. S. Miyada and A. L. Tappel. *Analytical Chemistry*, **28,** 909 (1956).— Factors specifically associated with the processes of color development have been investigated. The instability of the color developed in the method as given by Neuman and Logan limits the precision of the measurements. The present work shows (*a*) that if 1.5 *N*, 3.0 *N*, or 9.0 *N* sulfuric acid is added, the most intense color is formed with 3.0 *N*, but the best color stability is obtained with the addition of 1.5 *N* acid; (*b*) the optimum heat treatment is 80°C. for 30 minutes; and (c) although tyrosin and trytophan have maximum absortion spectra below hydroxyproline, yet there is a small interference effect if either of them is present with hydroxyproline in equimolar concentration. The recommended procedure is given in detail. H.R.W.

Indicator for Titration of Calcium in Presence of Magnesium Using Disodium Dihydrogen Ethylenediamine Tetraacetate. H. Diehl and J. J. Ellingboe. *Analytical Chemistry*, **28,** 882 (1956).—A new indicator, designated Calcein, has been prepared for the titration of calcium in the presence of magnesium with disodium dihydrogen ethylenediamine tetraacetate. No preliminary treatment is necessary beyond dissolving the sample and adjusting the pH to a value of 12. Excessively large amounts of sodium and magnesium cause the results for calcium to be slightly low. Interference of copper and iron is obviated by the addition of cyanide. Authors' abstract.

Factice-Formation as a Cause of Fat Spue on Leather. F. Stather and G. Königfeld. *Das Leder*, **7,** 35 (1956).—Sticky, resinous, flat or drop-like exudations on the grain or flesh sides of vegetable-tanned leather oiled with oxidizable fats, have long been known. Their origin has been ascribed to oxidation and polymerization of fat in the leather and the forcing of the oxidation or polymerization products through pores to the surface of the leather because of heat and increase in volume of the fat. A spue similar in appearance but caused by an entirely different reaction has been found. After storage in piles for a few months vegetable leather showed irregularly distributed exudations on the grain and flesh. These exudations were both small and large, usually round, and bright to dark brown. They were rather tough, rubbery, dry (not sticky) and were attached only in the middle at the point of exudation. On heating they melted with charring; they were insoluble in all organic solvents and gave a strong test for sulfur. These facts, which have been confirmed by further work, show that a factice-like material had separated from the leather. Such a spue was previously unknown. Factice is the product resulting from the vulcanization (by treatment with sulfur chloride or sulfur at elevated temperature) of a drying or semidrying oil such as linseed, poppy, cottonseed, castor, train, beet oil, etc. Its possible formation in leather containing sulfur was investigated by Abbassi (*JALCA*, **31,** 149). The leather reported on here was bated, pickled, treated with sodium thiosulfate, vegetable tanned, oiled warm with a 28% mixture of tallow, moellon, and train oil, bleached with oxalic acid, and the excess acid was neutralized with thiosulfate. It contained 9.7% moisture, 0.06% sulfur calculated from sulfate content of the ash, 0.6% sulfur extractable by carbon disulfide, 26.7% fat extractable by petroleum ether and 0.7% combined fat (Fahrion). The spue had a specific gravity of 1.03; it contained 1.7% of sulfur, was insoluble in organic solvents and water, and was saponifiable by potassium hydroxide. Factice must have been present within the leather also, where it may possibly improve water resistance, water absorption or resistance to wetting. Impregnation of leather with factice might be desirable. I.D.C.

The Reaction of Hide Substance and Aromatic Tanning, Dyeing and Auxiliary Materials. G. Otto. *Das Leder*, **6**, 207 (1955).—Previously the affinity between fibrous proteins and tanning, dyeing and auxiliary materials has been explained on the basis of two types of binding forces: (*a*) salt-type bonds between ions and (*b*) hydrogen bonds. These are not sufficient to explain all observations. Substances that cannot form hydrogen bonds are bound together more firmly than they should be by easily hydrolyzable salt-type bonds. Affinity is known to increase with molecular weight, but also non-aromatic acids have less affinity for wool than monosulfo acids of benzene and its derivatives. Aromatic nature imparts to an acid anion a unique, increased affinity for fibers that is greater the more expanded the aromatic system. The peculiarity of aromatic nature lies in the mobility of the π electrons in the system of conjugated double bonds. Such systems are easily polarized with formation of dipoles. Molecules with a dipolar nature form aggregates held together with considerable force. Methyl nitrite, CH_3-O-NO, boils at

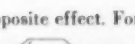
$-12°C.$, but nitromethane, $CH_3-N^{+}\begin{matrix}O\\ \diagup\\ \diagdown\\ O^{-}\end{matrix}$, at 101°C. The latter forms aggregates as follows:

$$\begin{matrix} R-N^{+}-O^{-} \\ O^{-}-N^{+}-R \\ R-N^{+}-O^{-} \end{matrix}$$

A stable 1:1 molecular compound is formed by dipoles of naphthalene and p-dinitrophenol. Picric acid is a known tanning material and has been used as a pretanning material, but it cannot combine by hydrogen bonds because the hydrogen is ionized. Its affinity must depend on dipoles. Phenol, which can form hydrogen bonds and has an affinity for the

$$-CONH- \quad \text{or} \quad -CON=$$

electron donor oxygen of the groups, lowers shrinkage temperature, Ts, in the acid and neutral pH range where dissociation of the phenolic group does not occur. This lower Ts and swelling of the hide is caused by breaking of existing hydrogen bonds between neighboring peptide groups in the chain molecule. Introduction of nitro-groups into the aromatic ring makes it more polar and provides more points for attachment. The close attachment to collagen increases the breaking of hydrogen bonds, but on the other hand, it prevents swelling of the hide, because it prevents attachment of water dipoles to the charged amino groups. In dinitrophenol the hydroxyl hydrogen is so highly dissociated that it can form bridges only in the pH range below 5. The dipoles induced by the nitro groups, however, form stable bridges between neighboring collagen molecules, knit them together, and, therefore, tan. The approximate distances, in angstroms, through which the various binding forces act, are as follows: electrovalent between anions and cations, 100A; between ions and permanent dipoles, 10A; hydrogen bonds, complex-forming forces and those between 2 permanent dipoles, 5A; Van der Waals forces between induced and permanent dipoles, or 2 temporary dipoles, 2 or 3A. Electrostatic forces draw the tanning or dyeing material to the collagen, after which the short range forces can act. The condensation product of formaldehyde with 2 molecules of paracresol tans, but its tanning ability is destroyed by introduction of one sulfo acid group in each ring. The 3-ring condensation product, however, which has tanning power, does not lose it but rather has it increased by the introduction of 2 sulfo acid groups. A strong electrostatic field extinguishes a neighboring weak polarity, but if the latter is further removed in a system of conjugate

double bonds, there is the opposite effect. For example, the sulfonic acid HO  SO_3H does not tan, but the acid HO CH_2SO_3H does tan. The role of anionic electrovalence, especially the sulfo group, in tannins, dyes, and wetting agents is as follows: (*a*) in the same molecule in a wide space it increases affinity for fibers by inducing dipoles and activating hydrogen for bond formation, but in a narrow space it lowers affinity because it covers (extinguishes) weak polar forces; (*b*) reaction with charged cationic groups of the fiber molecule increases fiber affinity first by attraction, after which the proximity of the partners permits weak polar forces to act; and reaction with the polar solvent (water) lowers affinity by a shell of water dipoles. Hydrotropic salts, as well as simple compounds like urea, are characterized by the presence of dipoles. They favor any existing tendency to form hydrogen bonds. Both types of force cause attachment of the hydrotropic portion of a molecule of a surface-active agent to the —CONH— and —CON= groups of collagen with splitting off of existing hydrogen bonds. They, however, can only build crosslinks between neighboring collagen chains if they are large enough or are sufficiently rich in weak polar forces. If they cannot form crosslinks and if they contain electrovalent groups which are not compensated by oppositely charged groups on the collagen, then the attraction of the ionic groups for polar water molecules will result in swelling and peptization of the collagen molecule. Considered in this light, hydrotropy appears to be a preliminary step, or more probably a requirement, for tanning. This idea is supported by the favorable action shown by numerous hydrotropic substances (pretannins) in promoting uniform deposition of vegetable tannin. Results with surface-active agents having sulfo groups may further clarify hydrotropic action. The following table gives data obtained by treating 10-gram portions of calfskin for 120 hours at 25°C. with 250 ml. portions of 0.2 molar solutions.

Sulfonic Acid Product	Rel. Capillary Activity	pH	Swelling (H_2O=100)	Ts (original =67°C.)	Collagen Dissolved %	Material After Drying
Beta-naphthalene-sulfonate	1	2	108	56	0.5	horny
		6.5	110	59	1.2	horny
Above condensed with formaldehyde	2.5	2	78	69	—	leather
		6.5	117	52	0.8	horny
Nekal A	24	2	107	52	0.7	rather horny
		6.5	132	47	2.2	gelatinized
Nekal BX	32	2	108	54	0.6	rather horny
		6.5	147	42	6.7	gelatinized
Dodecylsulfate	28	2	105	58	0.4	rather flexible
		6.5	135	53	0.8	horny
Dodecylbenzyl-sulfate	37	2	101	60	0.7	flexible
		6.5	142	49	4.2	horny

The formula for Nekals is where x is $—CH(CH_3)_2$ for Nekal A and $—CH_2—CH(CH_3)_2$ for Nekal BX.

There is considerable similarity between the presyntan beta-naphthalene sulfonate, with weak wetting power, and the wetting agents. In every case the hydrotropic effect was greater in neutral medium. The aromatic Nekals as free acids have a very weak tanning action. The dodecyl compounds have an oiling and softening action. To throw further light on the role of weak polar coordinate forces in the mutual reaction between wetting agents or dyes and collagen fibers, systems were investigated in which water-soluble compounds were added that had an affinity for the soluble component but none for collagen. Such compounds are polyethers whose ether oxygen acts as a donor for hydrogen bonds. These compounds are of low molecular weight compared to polyvinylpyrrolidone (PVP), which also shows affinity for dyes and an especially high affinity for extended systems of conjugated double bonds. PVP precipitates tannins that are free of sulfo groups. It contains in regular recurrence the —CON= group, which is an active dipole. The test was made by treating 10-gram portions of calfskin for 120 hours with 250 ml. portions of a 0.2 molar Nekal solution and varying amounts of either PVP (mol. wt. 9000) or Igepal (a polyether, mol. wt. 500). The attack on collagen by Nekal was retarded or prevented by both substances, but Igepal was more effective than PVP. The dye Direct Yellow B (mol. wt. 680) contains a chain of 11 conjugate double bonds. It has a high affinity for skin or chrome leather and so penetrates only slightly. Acid leather brown EGB has 4 isolated pairs of conjugate double bonds; it penetrates skin almost completely. The affinity of the yellow dye for skin is greatly decreased by PVP but scarcely altered by Igepal. On the other hand Igepal, even in small amounts, decreases the affinity of the brown dye for skin much more than PVP does. The attraction between PVP and the yellow dye is quite strong although the dye cannot form hydrogen bonds. Evidently the dye is so attached that the product remains soluble because of the sulfo groups of the dye. The force causing combination is to be found in the dipoles which also are the cause for stable, water-resistant compounds of Direct Yellow B and hide fibers. I.D.C.

Proteins of the Grain Membrane of Cattle Hide. S. R. Hoover, S. J. Viola, A. H. Korn, and E. F. Mellon. *Science*, **121**, 672–3 (1955).—This is a preliminary report. By treating steer hide or calfskin with strong acids, or by autoclaving them with water, the authors obtained the grain membrane in the form of continuous sheets, to which adhered a fine network of tissue from the lower layers of the corium. The yield was 1.0 ± 0.1 mg. per sq. cm., regardless of the thickness of the hide. The product contained 10.2 to 16.8% N_2, depending on the method of preparation, and 0.51–1.54% hydroxyproline. The low hydroxyproline content indicates that the proteins of the grain membrane, at least those resistant to hydrolysis, are not collagenous. The low cystine content (0.8%) indicates that little keratin is present. A positive test for carbohydrates was obtained with anthrone. The grain membrane proteins possess many similarities to elastin, but the presence of a dense, continuous elastin membrane is contrary to histological evidence. H.B.M.

Tube-shaped Structures of Collagen Fibrils. J. J. Kennedy. *Science*, **121**, 673–4 (1955).—Electron micrographs of sectioned fibrils from human periodontal membrane and rat tail tendon show pronounced tube-like structures. Under favorable conditions the 640 A. periodic striations are visible inside the tube. The same type of structure was observed in collagens from numerous diverse tissues. H.B.M.

Selective Acetylation of the Hydroxyl Groups in Gelatin. J. Bello and J. R. Vinograd. *J. Am. Chem. Soc.*, **78**, 1369–72 (1956).—Two methods are reported as being selective for the acetylation of the hydroxyl groups of gelatin: (*a*) treatment with acetic acid, acetic anhydride and perchloric acid and (*b*) treatment with acetic anhydride and trifluoroacetic acid. The completeness of the hydroxyl acetylation is determined by chemical

analysis for total acetyl, O-acetyl, and amino nitrogen. Additional evidence of the acetylation is furnished by the infrared spectra. In the two esterification methods reported, the strong acids inactivate the amino groups through salt formation and also catalyze the reaction of the anhydride with the hydroxyl groups. Trifluoroacetic acid inactivates both the amino and guanidino groups and catalyzes the acetylation, possibly through the formation of a mixed trifluoroacetic acid—acetic anhydride. Partial degradation appears to take place in both acetylation procedures as indicated by the reduction of intrinsic viscosity. Whether the degradation is due to the acetic anhydride itself, to the mixed anhydride, or to acetyl carbonium formed by ionization of the mixed anhydride is not clear, but it seems that the mixed anhydride alone does not cause degradation although it might do so in such a highly acidic medium as trifluoroacetic acid. H.R.W.

A Selective Stain for Elastic Tissue. H. M. Fullmer and R. D. Lillie. *Stain Technol.*, **31**, 27–29 (1956).—A selective stain for elastic tissue (designated orcinol-new fuchsin) is described. Two g. of new fuchsin (C.I. No. 678) and 4 g. of orcinol (highest purity) are added to 200 ml. of distilled water and the solution boiled for 5 min. Then 25 ml. $FeCl_3$ solution (U.S.P.1X) are added and the solution is boiled 5 min. longer. The precipitate is collected and dissolved in 100 ml. 95% ethanol. This is the staining solution. Sections are deparaffinized and brought to absolute ethanol, stained for 15 min. at 37°C. with orcinol-new fuchsin, differentiated for 15 minutes in 70% ethanol, dehydrated, cleared, and covered as usual. H.R.W.

Non-aqueous Titration Technique. III. Determination of Acid Radicals in Syntans. Y. Nayudamma. *Bull. Central Leather Research Inst., Madras*, **2**, 197–203 (1956).—A 0.2–0.5 g. sample of syntan is dissolved in 55 ml. of a solvent mixture containing 20 parts pure ethylene glycol, 15 *n*-butanal and 20 benzene, and titrated potentiometrically with 0.1 *N* NaOH in the same solvent mixture. The NaOH is standardized against 0.1 *N* HCl and 0.1 *N* acetic acid, also in the solvent mixture, and a blank is run on the solvent. The titration curve of cresol sulfonic acid had only one inflection point. When H_2SO_4 was added, a second inflection point was found, corresponding to ionization of the 2nd H+ of H_2SO_4. Addition of acetic acid gave yet a third inflection point. Thus it was possible to distinguish between "stronger" acids (HCl, HNO_3, sulfonic acid, and the first ionization of H_2SO_4) which are titrated completely at an apparent pH of about 3, "strong" acids (second ionization step of H_2SO_4 and first of oxalic acid) titrated completely at pH 5, and weak acids (second ionization step of oxalic acid, acetic, formic, etc.) titrated completely at pH 7. Phenolic OH groups are not titrated. In products of known history it is possible to determine the individual acids quantitatively. The products of sulfonation of cresol with 35 and 60% H_2SO_4 contained no free H_2SO_4, while products made with 90 and 100% H_2SO_4 contained 0.9–1 mg.-equiv. free H_2SO_4 per g. of product. Interpretation of the titration curves of commercial syntans (of which 14 are given) is more difficult, because the strength of the acid radical is affected by its position in the molecule and by neighboring substituents, and only the totals for "stronger", "strong", and weak acid radicals can be determined. The effects of various condensation treatments on the titration curves are illustrated. H.B.M.

New Barks for E. I. Tannage. I. Peltophorum Ferrugineum. M. K. Udaya Varma, E. C. Mathew, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **2**, 204–9 (1956).—This tree (local names "Iyalvagi" and "Kondocinta") is abundant in S. India. A bark sample contained H_2O, 7.8%; tannin (catechol type), 20.8%; soluble non-tannin, 9.5%; insolubles, 38.1%; ash, 6.6%; sugars (as glucose), 3.8%; free acid (to pH 5.8), 8 mg.-equiv. per 100 g. soluble matter; total salts (resin exchange method), 73 mg.-equiv.;

pH of analytical solution, 5.0. The titration curve of this extract is very similar to wattle, but the extract contains more salts of weak acids and is better buffered. Tanning tests were made with cow sides, using *P. ferrugineum* bark, alone or blended with myrobalans or "Konnan" bark, in a conventional E.I. tanning process. The resulting leathers compared favorably with control sides tanned with a blend of konnan bark and wattle extract, with respect to general appearance and color. Tightness, fullness, and yield values were the same for the experimental and control leathers. This bark may prove a good substitute for wattle. H.B.M.

The Introduction of Tanning Machines in the Beamhouse. A. Brill. *Das Leder*, **7**, 25 (1956).—A general discussion of fleshing machines and of methods for speeding beamhouse operations. I.D.C.

BOOK REVIEWS

Bibliography of Solid Adsorbents, 1943 to 1953 (National Bureau of Standards Circular 566). V. R. Deitz. Government Printing Office. 1956. 1525 pp. $8.75.—This ponderous collection of 13,763 annotated references is a joint project of the Bureau of Standards and the Bone Char Research Project, Inc. Included are some 20 papers on various phases of the chemistry and physics of leather, some of which have no discernable connection with solid adsorbents. The compilation seems to have been thoroughly and carefully done, and the work will undoubtedly be of great value to workers in many fields—not, however, in leather chemistry. A previous volume covered the literature from 1900 through 1942. H.B.M.

Analytical Reviews. *Anal. Chem.*, **28,** No. 4, Part 2 (1956).— This year's annual issue presents 29 fundamental reviews authored by 42 nationally and internationally known experts. A glance at the table of contents indicates the wide adaptation of instrumentation to chemical analytical methods. Each review is followed by a very comprehensive list of literature citations which will prove most valuable to all readers. The reviews of broadest interest to leather chemists are: Instrumentation, Chromatography and Electrochromatography, Inorganic Gravimetric and Volumetric Analysis, Volumetric and Gravimetric Analytical Methods for Organic Compounds, Biochemical Analysis, Extraction, Ion Exchange, Inorganic Microchemistry, Organic Microchemistry, and Statistical Methods in Chemistry. H.R.W.

The East African Hides, Tanning, and Allied Industries Bureau Report for 1954. Nairobi, East Africa. 1955.—Received, but not reviewed.

Annual Reviews of Biochemistry, Vol. 24. Stanford, Cal.: Annual Reviews, Inc. 1955. xvi + 805 pp. $17.00—Reviewed in *J. Am. Chem. Soc.*, **78,** 1075 (1956).

The Chemistry of Tanning Processes. K. H. Gustavson. New York: *Academic Press.* 1956. ix + 403 pp. $9.00.—The author states that his aim is to give a general outline of the chemistry of the principal tanning processes in the light of modern concepts of tannages. Practical details are not discussed as a rule, and the preference is given to discussion of chromium and vegetable tannages and their combinations with each other and with other tannages. Within the limits he has set for himself, Dr. Gustavson has prepared a critical

appraisal of our current knowledge, an appraisal which is strengthened by his active participation in the development of this knowledge.

The chemistry of chrome tanning salts and the application of this chemistry to tanning theory are considered in 140 pages. Plentiful literature citations, tables and figures contribute to one of the best discussions of chrome tannage which is available in English. It seems however that the author has somewhat missed the significance of the use of formates in American tannery practice. Vegetable tannage is discussed less comprehensively, with 100 pages being devoted to natural vegetable tannins, syntans and lignosulfonates and their reactions with collagen. The remainder of the book includes shorter discussions of aldehyde, quinone, and oil tannages and combination tannages. The book ends with an interesting, thought-provoking 30-page chapter on tanning reactions of biological and medical importance.

The book is prepared in Academic Press's usual careful style of binding and printing, with good-quality book paper being used. Topical chapter outlines used as the table of contents and 28 pages of author and subject indices aid in the use of the book. The reviewer has found very few errors, although literature reference 17 on page 141 contains an incorrect page reference.

Coupled with its companion volume, entitled *Chemisty and Reactivity of Collagen*, which the same author and publishers have just issued, this book presents a thorough, authoritative discussion of much of the current theoretical literature in tanning chemistry. This reviewer particularly enjoyed the evidences of the vigorous personality and scientific acumen of the author; and it is certain that Dr. Gustavson's personal, critical appraisal of our knowledge will "stimulate the further inquiry into these intricate reactions" which intrigue and plague all of us. R. M. Lollar

The Chemistry and Reactivity of Collagen. K. H. Gustavson. New York: *Academic Press.* 1956. ix + 342 pp. $8.00.—As he states in his Preface, and as is well known to his many friends in the United States, Dr. K. H. Gustavson, Director of the Swedish Tanning Research Institute, has worked with collagen in the form of hides and skins for nearly four decades. This extensive experience forms the background for the present book, in which the author has given a comprehensive discussion of the chemistry of this important protein. It has been his principal objective to fill in the existing lacunae in the available books on collagen, with particular reference to its chemical behavior in reversible aqueous systems. In this endeavor he has succeeded very well. From the standpoint of the leather chemist, the book may be said to deal primarily with reactions important in pretanning processes. Although considerable material dealing with modern physicochemical concepts of tanning mechanisms is given, this subject is treated in much more detail in the companion volume, *The Chemistry of Tanning Processes*, also reviewed in this issue of the Journal.

The book begins with a chapter giving a brief, but adequate, outline of general protein chemistry, including a description of modern chromatographic analytical methods and of structural features common to proteins in general. This is followed by a chapter describing the histological features of the skin and some general aspects of the structural organization of the fibrous proteins. The chemical composition of collagen is discussed in some detail. Chapter 3 is devoted to a consideration of the various structural studies of fibrous proteins in general, and of collagen in particular, by X-ray diffraction, optical, and electronoptical methods. An account is given of the development of modern concepts of helical polypeptide chain configurations. It is unfortunate that the book appeared too early to permit any mention of the recent three-chain helical models, which at the present time appear to point the way to a complete solution of the long-vexing problem of collagen structure, particularly so as Dr. Gustavson's own contribution to the interchain bond structure (the hydroxyproline hydroxyl-carbonyl link) has played such an important role in their development.

The heart of the book is in the next seven chapters, entitled, respectively: The Isoelectric Points of Collagen; The Interaction of Collagen with Acids and Bases and the Titration

Curves of Collagen; The Internal Linking of the Collagen Molecule; Swelling of Collagen, Donnan Effect; Lyotropic Effects; The Contraction of Collagen, Particularly Hydrothermal Shrinkage and Crosslinking Reactions; and Inactivation of Specific Groups of Collagen for the Study of its Reactivity. In these sections, covering some 170 pages of text with charts, diagrams, and tables, much detailed information on the reactivity of collagen is set forth. A great deal of this is the author's own work, but the field is covered thoroughly, and the reviewer is not aware of any other single treatment of such a comprehensive nature. In the next two chapters the action of proteolytic enzymes on collagen and leather, and the chemistry of unhairing and of the conversion of collagen to gelatin, are discussed. The final chapter deals with some physicochemical aspects of the reactions of collagen with tanning agents. All through the book abundant references to the original literature are given, and the work has considerable value as a source book for this reason.

The typography and binding are in the publisher's usual attractive style, and misprints appear to be relatively few. Adequate subject and author indexes are provided. The price, while appearing to be somewhat high, is not out of line with comparable scientific books of recent vintage.

This book appears at a time when interest in collagen in scientific circles might be said to be running at fever pitch. The importance of this unique protein these days far transcends its role in the technological processes of tanning and glue and gelatin manufacture. From an obscure position in the background collagen has suddenly assumed the center of the stage, and it now seems quite likely that within the next few years it will have suffered an almost magical transformation from one of the least understood to one of the most completely understood of the proteins. To the development thus foreshadowed Dr. Gustavson's own work has contributed in no small measure, and it is to be expected that the present book will provide a valued aid to the workers in the field. Any chemist having a serious interest in the chemistry of collagen will want it on his library shelf. J. H. Highberger

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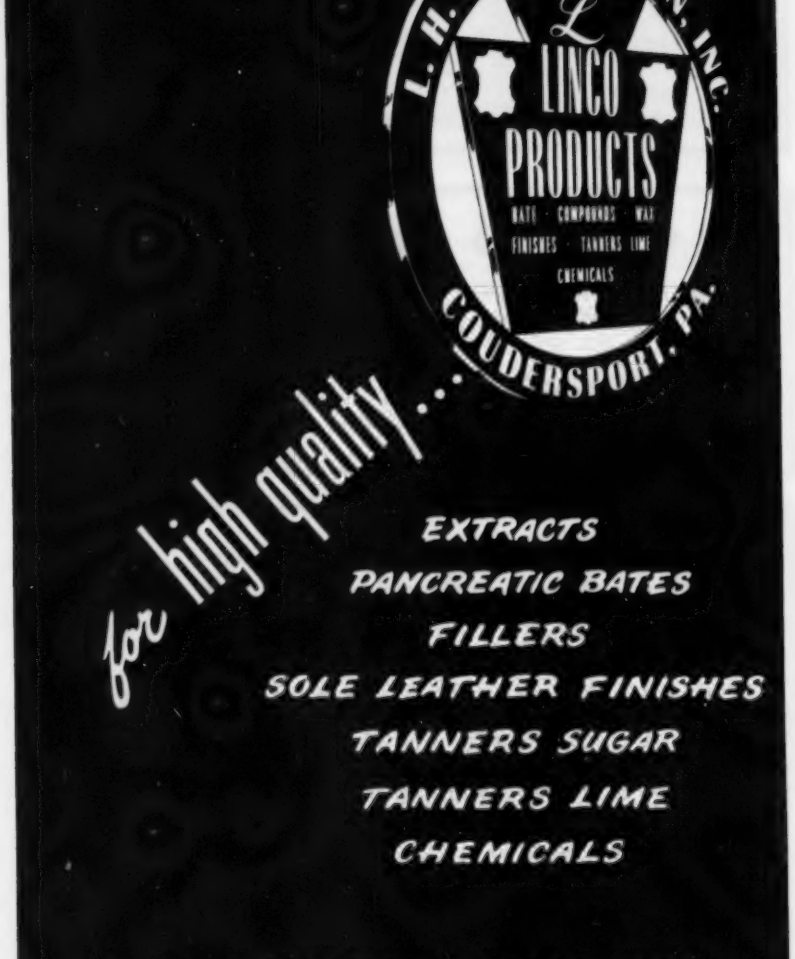
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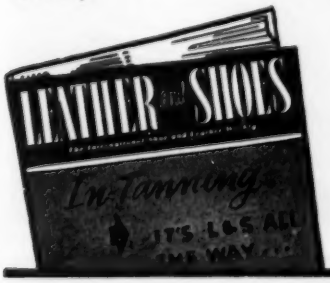

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